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COO-3514-1

ION MOBILITY IN MOLTEN SALTS

Final Report

Richard W. Laity

Rutgers University

New Brunswick, New Jersey

September 1, 1965 - August 31, 1971

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION

UNDER CONTRACT NO. AT(11-1) - 3514

(FORMERLY NO. AT(30-1) - 3608)

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Ion Mobility in Molten Salts

Abstract

The general objective of this program was to gain an understanding of the factors controlling the rates at which ions in molten salts move under the influence of applied forces. This was being accomplished through experimental study of specific molten salt systems, accompanied by theoretical interpretation of results obtained both in this laboratory and elsewhere.

Progress has been made in number of areas, including "concepts of ion mobility", characteristics of mobility in pure salts, significance of external mobilities, and characteristics of mobility in binary salt mixtures. Of particular significance was the discovery (and interpretation) of the very strong concentration dependence of the relative electrical mobilities of two cationic species in simple binary mixtures. This effect has been found to be much larger than the corresponding behavior of diffusion mobilities. Like most other observations in the areas listed, however, this characteristic of molten salt mobilities has not yet been given a generally accepted or definitive explanation. The report therefore concentrates on experimental developments, with some speculation as to their significance.

The text summarizes activities during the entire period of this contract and its predecessor AT(30-1)-2644 carried out at Princeton University. Included along with the foregoing is a comprehensive evaluation of progress in the general area of ion mobility in molten salts.

Although emphasis will be given to results obtained in this program, discussion of relevant results obtained elsewhere will be included. For background of a general nature the reader is referred to two excellent reviews recently published, dealing with the field of molten salts generally (1) and with ionic transport in molten salts (2).

I. General objectives. The purpose of the program was to gain an understanding of the factors controlling the rates at which ions in molten salts move under the influence of applied forces. This was being accomplished through experimental study of transport properties of specific molten salt systems, accompanied by theoretical interpretation of results obtained both in this laboratory and elsewhere. Of particular interest are properties that depend upon the relative rates at which different ionic species move when present together in the same melt. Due to the arbitrariness of attempts to assign relative electrical mobilities to oppositely charged ions (see below), a major effort has been devoted to processes involving relative motions of like-charged ions in a simple binary mixtures. Phenomena included in this category are conductivity, transference and diffusion. By studying the concentration dependence of such properties it has been possible to observe the effects of continuous variations in the nature of the system, thus obtaining insights which could not be gained from a study of pure salts only. The possibility of achieving correlation with equilibrium properties has also been

enhanced through this approach, since the thermodynamic behavior of such mixtures is better understood (in the sense of being able to make accurate predictions) than the equilibrium properties of pure components taken individually. For this reason the focus of this effort has been concerned primarily with systems whose structural and thermodynamic properties seem to typify characteristic behavior of simple classes of ionic melts.

The other major effort has been directed toward understanding concepts of ion mobility itself as they pertain to completely ionic systems, and to interpreting the significance of the various experiments by which quantities purporting to be indicative of the mobilities of specific ions in molten salt systems have been determined.

II. Concepts of Ion Mobility. The concept of diffusion mobility is operationally distinct from that of electrical mobility even in electrolytic solutions, where the former is measured by a tracer-diffusion experiment and the latter obtained from a combination of conductivity and transference data. Both involve the arbitrary choice of a reference with respect to which ionic velocity is measured, but only in the case of diffusion is there a "natural" or unequivocal reference for molten salts systems (3).

Electrical mobility. In the work carried out under this program, the problem of assigning electrical mobilities has been dealt with in two ways: (a) Equations based on the principles of irreversible thermodynamics have been used to define mobilities in terms of phenomenological coefficients relating ionic fluxes to applied gradients of electrochemical potential. A frame of refer-

ence can be established by introducing suitable auxiliary equations in which the superfluous coefficients are removed according to a scheme that forces the remaining quantities to have a form consistent with that which one might anticipate from a mechanistic picture of the transport process. This approach makes it possible to assign electrical mobilities on the basis of self-diffusion and conductivity measurements alone (4). (b) In mixtures containing two like-charged ions but only one species of the opposite charge, the latter can be taken as reference in comparing relative mobilities of the former during electrolysis (5). It is important to realize that this approach yields mobility differences, rather than ratios. A lower limit on the ratio can be obtained by assuming the reference ion cannot have an "absolute" mobility less than zero. Even so reasonable an assumption as this one might be challenged on the basis that certain ions have been found to exhibit negative transport numbers in very concentrated aqueous solutions of their salts. It is clear, nevertheless, that at least one of the like-charged ions can be assigned a positive mobility unequivocally, so that such experiments leave no doubt as to which of the ions being compared migrates faster in the direction of the appropriate electrode.

Progress employing approach (a) warrants further elaboration in this section. The first method of assigning electrical mobilities to the ions in pure molten salts from the results of self-diffusion and conductivity measurements only was proposed at the Faraday Society Discussion on Ionic Melts in 1961 (4). The arbitrary choosing of an external reference frame was avoided by allowing the transport properties of the system to dictate an appropriate frame

implicitly. Equations developed as part of this program were used to define ionic transport parameters phenomenologically which consisted of diffusion mobilities "corrected" by a quantity aimed at taking into account the interference between opposing ionic flows. Electrical mobilities could thus be calculated for any pure salt from experimentally obtained self-diffusion coefficients, combined with the equivalent conductance of the salt. Values obtained in this way were used to calculate transport numbers of ions in salts for which appropriate data were available. It was pointed out that the ultimate virtue of such quantities must depend on their ability to yield correlations among independently determined properties, macroscopic and/or microscopic. As an example, these "internally" determined quantities were compared with the data available on "external transport numbers", quantities measured relative to porous plugs or "paper" strips. Even though the significance of the latter quantities has been called into question by work to be described shortly, it appeared on the basis of the data that some such correlation may exist between these operationally unrelated assignments of electrical mobility.

Since that time, the amount of data available for such comparisons has increased significantly, and some of the figures employed then have been improved upon. Perhaps at least as important has been the recognition that the formalism originally proposed was not the only way simple phenomenological equations could be designed to yield electrical mobilities consistent with reasonable speculations about the reasons for the observed deviations of molten salts from the Nernst-Einstein relation. Specifically, diffusion mobil-

ities in the original formalism were "corrected" by subtracting the same quantity from both positive and negative ion fluxes. This kind of correction is appropriate for the model of Borucka, Bockris and Kitchener, who assume a coupling between cation and anion fluxes (6). It seemed at least as plausible, however, to consider the mutual interference between opposing flows during electrolysis as a force that would result in equal and opposite reductions of the net forces applied to the two ionic species. To set up equations consistent with this concept it was necessary to apply a correction to the thermodynamic force on each ion proportional to the magnitude of the relative ionic velocities (7). The resulting equations were used to calculate a new set of transport numbers which can be distinguished from those previously calculated by the name "force-corrected transport numbers", the earlier quantities being designated as "flux-corrected". Table I provides a comparison of some values of these quantities with one another, and with external transport numbers reported in the literature (8). Although not all data employed in constructing the table are regarded as equally reliable, it appears that there may be significant correlation among all three types of transference numbers for most of the salts listed. In spite of the slightly better agreement between the flux-corrected quantities and the external values, it would be premature to rule out the force-corrected transference numbers as the more significant quantities. The significance of external transference numbers has not been adequately elaborated, and in view of the double-layer effects to be described, it may ultimately be necessary to modify the values listed in Table I. In the meantime, we point

TABLE I
Cation Transport Numbers in Pure Fused Salts (8)

Salt	Temp. °C	t_+		
		External	Flux- corrected	Force- corrected
LiCl	610	0.75	0.77	0.68
NaCl	800	0.62	0.73	0.59
K Cl	830	0.62	0.54	0.53
RbCl	785	0.58	0.54	0.53
CsCl	705	0.56	0.47	0.48
TlCl	630	0.47	0.47	0.48
LiNO ₃	350	0.84	0.80	0.72
NaNO ₃	350	0.72	0.66	0.61
K NO ₃	350	0.57	0.53	0.53
CsNO ₃	450	0.48	0.51	0.50
AgNO ₃	350	0.72	0.66	0.63
CaCl ₂	800	0.42	0.57	0.59
SrCl ₂	900	0.26	0.47	0.51
BaCl ₂	1000	0.23	0.44	0.44
ZnCl ₂	500	0.66	0.44	0.62
ZnBr ₂	500	0.75	0.54	0.61
CdCl ₂	590	0.66	0.69	0.68
PbCl ₂	600	0.24	0.46	0.52
PbBr ₂	500	0.36	0.52	0.58

out that force-correction is exactly what is done in the Debye-Hückel-Onsager treatment of electrolytic solutions, while flux-correction corresponds to postulating the existence of ion pairs. The latter approach has greater flexibility, since combinations other than simple pairs can be postulated and mobilities assigned arbitrarily to the resulting complex ions. Unless the same quantities can be obtained independently by other methods, however, this would simply add to the already confused status of complex ions in molten salts, and amount to little more than a reexpression of experimental data. On the other hand, the usefulness of the force-correction approach might be tested in part by calculating the corresponding quantities in electrolytic solutions as functions of concentration to ascertain their behavior outside the region of validity of the Debye-Hückel-Onsager theory.

Diffusion mobility. In addition to the concept of diffusion mobility represented by "self-diffusion" coefficients, the study of mixtures makes it possible to determine other operationally defined quantities such as those called "ordinary" and "chronopotentiometric" diffusion coefficients. Rigorous equations of nonequilibrium thermodynamics were used in this research to establish unequivocal phenomenological relations among these quantities, revealing the fact that all three diffusion coefficients become identical at infinite dilution (9).

Friction coefficient formalism. An alternative to simple ion mobility is the concept of "interionic friction" originally proposed by Klemm (10). In the present program phenomenological equations of nonequilibrium thermodynamics were developed which provide friction

coefficients that can be calculated from the results of conventional transport experiments (11). This approach has the potential advantages that (a) all velocities are measured relative to those of other species in the system, and (b) the rate parameters obtained are all expressed in the same dimensions (thereby making them directly comparable with one another). It is hoped that such comparisons may lead to useful discoveries (correlations). Thus far, a proposal to use the observation of negative friction coefficients as a criterion for ion association appears to be consistent with conclusions based on other types of data (12), and it has been shown that the friction-coefficient formalism can be of considerable value, both conceptually and mathematically, in dealing with diffusion-migration problems requiring only a macroscopic point of view (13).

III. Characteristics of Mobility in Pure Salts. Under this heading will be considered only the self-diffusion mobilities (as characterized by ionic tracer-diffusion coefficients) and internal electrical mobilities (represented by the salt conductances Λ , since one species is taken as reference in assigning a velocity to the other). Accurate values of the latter quantities are more easily obtained experimentally, than the former, especially under the handicaps imposed by making the measurements at high temperatures. Impurities introduced by corrosion and decomposition, and even by hydrolysis and direct reaction with oxygen in melts not adequately protected from exposure to air, can have disastrous effects on any such measurements, however, so that even results exhibiting high precision must be critically evaluated.

Conductance measurements. As a part of the present program, apparatus was constructed for making very precise ($\pm 0.1\%$) conductivity and density measurements in molten salt systems at temperatures up to 1000°C . The latter measurements, as well as less precise determinations of surface tension (when a density bob method is used), are necessary to convert from specific to equivalent conductance. Preliminary efforts were aimed at establishing the reliability of the equipment and ascertaining the importance of purification procedures in the study of molten alkali halides. Extensive pretreatment aimed at avoiding the presence of water or hydrolysis products in the melt was applied before carrying out measurements of both κ and ρ for a number of alkali halides over significant ranges of temperature. Results were generally in good agreement with the classic work of Van Artsdalen and Yaffe (15), but revealed some small discrepancies (up to $\pm 5\%$) subsequently confirmed by other workers (16, 17). Effects of frequency dispersion on the measured values of κ were small (especially at 1000, 2000, and 5000 hertz), but agreed with the later considerations of Braunstein and Robbins (18).

Dependence of mobility on ionic properties. Conductance results for pure salts obtained in the present program will not be described further at this point, since the characteristics of concern here are best observed by examining some of the many reliable results reported by other workers. Such reports, along with the increasing number of self-diffusion coefficient determinations appearing in the literature, have provided this program with a large reservoir of essential information.

For illustration, a collection of values of both D_i and Λ for a variety of pure salts at specified temperatures is presented

in Table II. Of particular note are the following observations:

(a) The overall range of Λ values calculated on the assumption of complete ionization is less than two orders of magnitude, indicating that the degree of ionization in all salts listed must be substantial, if not complete. (No unambiguous criteria for degree of ionization in molten salts have been put forward, but Moynihan has invoked the combination of high fluidity and low conductivity as a qualitative indicator of incomplete ionization (2).)

(b) The diffusion mobility of chloride ion in alkali halides at 800°C is not very sensitive to the nature of the alkali cation with which it is associated, nor does the diffusion mobility of nitrate ion at 350° vary strongly in its combinations with Li^+ , Na^+ , K^+ and Ag^+ . In this connection the assertion of Angell and Helphrey that alkali nitrates at the same temperature are in very nearly "corresponding states" should be noted (19).

(c) The diffusion mobilities of the alkali cations in a given series decrease with increasing cation radius (but the values for all these cations in molten nitrates are rather small compared to that of Ag^+ when ion sizes based on Pauling's crystal radii are compared). The figures in Å units are as follows: Li^+ (0.60), Na^+ (0.95), K^+ (1.33), and Ag^+ (1.26).^{*} For univalent cations

^{*}A recent paper by Masterton, Bolocofsky and Lee [*J. Phys. Chem.*, 75, 2809 (1971)] presents persuasive evidence (based on scaled particle theory of the salt effect in aqueous solutions) for replacing the Pauling values by the following: Li^+ (0.74), Na^+ (1.01), K^+ (1.32). New figures are not provided for Ag^+ , but Blander favors taking its radius in molten nitrates equal to that of Na^+ (20). This would appear consistent with the fact molten AgNO_3 and molten NaNO_3 have substantially identical molar volumes, and would account for the "anomalous" value of D_{Ag^+} , but appears to suggest that it may not be possible to assign unique radii to some species — a situation that would weaken the utility of the radius concept.

TABLE II

Self-Diffusion and Conductance in Some Pure Fused Salts (8, 14)

Salt	Temp. °C	$10^5 D_+$ (cm ² /sec)	$10^5 D_-$ (cm ² /sec)	Λ (cm ² /eq. ohm)
NaCl	800	7.38	5.83	134
KCl	800	7.14	6.35	110
RbCl	800	5.83	5.13	95.2
CaCl ₂	800	2.15	2.97	56.4
LiNO ₃	350	2.93	1.15	53.0
NaNO ₃	350	2.33	1.48	52.7
KNO ₃	350	1.52	1.35	35.9
AgNO ₃	350	2.40	1.40	55.7
ZnCl ₂	500	0.27	0.33	2.66
ZnBr ₂	500	0.134	0.172	2.76
PbBr ₂	500	1.07	1.57	33.4

(except possibly Ag^+) the sequence is thus in qualitative accord with that predicted by the Stokes-Einstein equation, assuming the bare (uncomplexed) ion plays the role of the "hard sphere" employed in its derivation. It is well known that the sequence of mobilities of the same cations exhibits exactly the opposite trend in aqueous solutions at infinite dilution (where diffusion and electrical mobilities are identical except for dimensions, since the Nernst-Einstein relation is rigorously obeyed). The obvious interpretation is that the "hydration sphere" induced by the high field of the central ion renders the actual unit of transport (hydrated ion) larger when its charged-sphere radius is smaller (21). This is quantitatively consistent with the fact that the "Stokes radii" calculated from the aqueous mobilities are substantially larger (by 0.5 to 3 Å) than the corresponding crystallographic radii for all the cations listed. For the univalent anions Cl^- , Br^- and I^- , aqueous Stokes radii are calculated to be smaller than crystallographic, showing unequivocally the quantitative inapplicability of Stokes' model to "spheres" of dimensions comparable to those of the structural units of the liquid (water molecules). It is of interest to note that in most molten salts, Stokes radii calculated for univalent ions from self-diffusion coefficients like those listed in Table II are also smaller than crystallographic radii. In spite of the quantitative inapplicability of Stokes' model to such cases, this observation, considered alongside the corresponding behavior of Stokes radii in aqueous solutions, seems to imply that single ions (rather than complex species or "groups") constitute the units of transport (moving entities) in such melts. (However, some evidence for an apparently

conflicting viewpoint will be mentioned below in considering the observed mass dependence of ion mobility in molten salts.)

(d) In the salts containing divalent cations, diffusion mobilities of both species are seen to be generally smaller than in the 1-1 systems. It is evident that ionic motion must be restricted in the presence of the extreme fields associated with such cations. Viscous flow is also inhibited, however, so that the Stokes radius of Cl^- in molten CaCl_2 at 800°C is almost identical with its corresponding value in NaCl . If the somewhat larger Stokes radius of Ca^{+2} is now attributed to some sort of association (analogous to hydration in aqueous solutions), it is difficult to see why such association does not affect the mobility of Cl^- accordingly. This appears to be a basic problem in the understanding of molten salt transport for which a satisfactory solution has yet to be proposed.

Further examination of the figures for salts with divalent cations reveals that diffusion mobilities in the zinc halides are smaller by almost an order of magnitude than in the more typical example of PbBr_2 at the same temperature. Some kind of network association appears indicated by the correspondingly high viscosity of these rather exceptional salts. Such "chemically" based extremes of transport behavior demonstrate unequivocally that simple charge-related coulombic forces (ionic bonds) in conjunction with possible steric considerations of ionic size are not sufficient to account quantitatively for observed mobilities in molten salts. The catch-all concept of "covalent character" does little to relieve the situation, however, except in even more extreme cases like the mercuric

and aluminum halides where $\Lambda < 10^{-2}$, but fluidity is high. By contrast, the diffusion mobility of Ag^+ in the molten silver halides is as large or larger than that of Na^+ in the presumably less "covalent" sodium halides at the same temperatures.

(e) The preceding generalizations have focussed primarily on diffusion mobilities, since no arbitrary reference frames are introduced in the experiments by which individual ionic values are assigned. (The salt itself serves as reference, just as the bulk liquid does for tracer-diffusion/in non-electrolytes.) As a final generalization, however, it should now be noted that the "internal mobility" specified by the value of Λ in each salt, exhibits characteristics remarkably parallel to the net behavior the two ionic diffusion mobilities. This is equivalent to stating that even though the Nernst-Einstein relation does not apply quantitatively to molten salts (22, 2), the total conductance behaves as though it were made up of a sum of ionic components ($\Lambda = \lambda_+ + \lambda_-$). The problem of assigning values of the λ_i operationally was briefly reviewed in the foregoing; the present statement is included primarily to show how the observed behavior of Λ in pure fused salts, in comparison with that of D_+ and D_- , appears to justify the search for suitably defined quantities λ_+ and λ_- in the absence of a "natural" or "logical" frame of reference.

The effect of ionic mass on electrical mobility has received considerable attention in the form of isotope-separation experiments based on differential rates of electromigration. The results of such experiments can be characterized by the "mass-effect" μ_i defined as

$$\frac{\Delta u_i}{(u_i)_{av}} \bigg/ \frac{\Delta m_i}{(m_i)_{av}} \quad \text{where } u_i \text{ is the mobility of the lighter isotope and}$$

m_i its mass. In most experiments the reference for u_i has been the oppositely charged ion, so that such results should be called "internal mass effects". Some "external mass effects" have also been measured on "paper strip" reference materials of suitable refractory fibers. The latter quantity is related to the former by

$$\mu_i(\text{ext}) = \frac{\mu_i(\text{int})}{t_i(\text{ext})}$$

where $t_i(\text{ext})$ is the external transport number of i . If attention here is confined to results obtained for $\mu_i(\text{int})$ in pure salts, several generalizations seem to emerge from available data for more than twenty cases - mostly halides, but including some nitrates. (a) The value of μ_i is always negative (heavier ^{isotope} / migrates more slowly), as might be anticipated from any crude theory of transport; its absolute value lies somewhere between 0.01 and 0.2. (b) Although not strongly temperature dependent, $|\mu_i|$ usually increases with increasing temperature. (c) In a series of salts having different cations (or anions) and a common anion (or cation), the value of μ_+ (or μ_-) becomes smaller as the mass of the cation (or anion) increases. (As long as the series have common "classes" of cations (or anions), like the alkali metals or any particular sub-group in the periodic table, there are no known exceptions to this rule.) (d) In halides (Cl^- , Br^- , I^-) having a common cation, $|\mu_+|$ increases with increasing mass of the halide ion. Conversely, in a series (periodic group) of salts with a common halide anion, $|\mu_-|$ increases with increasing mass of the cation. Exception: in ZnCl_2 , $\mu_- = -0.043$, while in CdCl_2 , $\mu_- = -0.030$. It must be borne in mind, however, that there is considerable

variation in the reliability of the data. This fact is most evident when one compares recently determined μ_i values with previously reported figures for some of the same salts (23, 24).

Klemm has provided some rationalizations for the observations noted above (23). He first asserts that from the kinetic theory of gases, a dilute gas composed solely unassociated cations and anions would have the theoretical values

$$\mu_+ = - \frac{1}{2} \frac{m_-}{m_+ + m_-}$$

and

$$\mu_- = - \frac{1}{2} \frac{m_+}{m_+ + m_-}$$

In the absence of a more refined model for molten salt migration, one can try applying these equations to experimental μ_i values. It is apparent that generalizations (a), (c), and (d) are all predicted by the dilute gas model. Quantitatively, however, the experimental values are always much smaller than those calculated from the equations. Klemm interprets this as evidence for "coupling" of ionic motions in the liquids. Coupling would reduce the effective value of the fractional change $\Delta m_i / m_i$ in mass of the moving species. At temperatures far below the critical point, ionic coupling should decrease with increasing temperature, a prediction verified by generalization (b). Perhaps the most dramatic evidence introduced in support of the "coupling" concept was Klemm's comparison of μ_+ for $^7\text{LiCl}$ containing traces of $^6\text{Li}^+$, with the total conductance change in going from $^7\text{LiCl}$ to $^6\text{LiCl}$ (25). From the latter results he calculated the quantity μ_+^o defined by $\frac{\Delta \Lambda}{\Lambda} / \frac{\Delta m}{m}$ in which $\Delta \Lambda / \Lambda$ can be

taken equal to $\Delta x/k$ within experimental error. It turned out that $\mu_+^0 = -0.34$ in LiCl, compared with a figure of -0.11 for μ_+ in $^7\text{LiCl}$. One way of accounting for this difference is to postulate that the motion of each Li^+ ion is coupled with that of two of its nearest Li^+ neighbors. The $\frac{\Delta m}{m}$ for such a "group" of three $^6\text{Li}^+$ would thus be three times as great as that for a group that contained one $^6\text{Li}^+$ tracer ion along with two $^7\text{Li}^+$ host ions such as would be found in the doped $^7\text{LiCl}$. Klemm noted further that the postulated reduction in degree of coupling with temperature was also borne out by a reduction in the ratio μ_+^0/μ_+ with increasing T . Whether or not one accepts Klemm's interpretations, it appears that he has made a highly significant discovery.

Dependence of mobility on temperature and pressure. The discussion thus far has concerned possible correlation between the mobility of an ion and the microscopic parameters by which are characterized its properties and the structures in its immediate vicinity. Much can be inferred about the nature of ionic transport, however, by studying the effects/^{of}externally controlled variables - temperature and pressure - on the mobilities of ions in representative systems. It would not be appropriate to attempt in this report a complete exploration of areas so intensively researched and discussed in the literature for so many years. Instead, this section will deal only with background specifically relevant to the activities of this program.

By now everyone is familiar with Angell's demonstration that the Arrhenius equation as applied to ionic mobility

$$\text{mobility} = (\text{const.}) \exp (E^\ddagger/RT)$$

where "mobility" may refer to any number of transport parameters

including A , λ_i , D_i and even the fluidity of the melt, does not apply to supercooled liquids (26). Instead, an equation of the form

$$\text{mobility} = A \exp [B / (T - T_0)]$$

was shown to describe the temperature dependence of such parameters over a considerable region of temperature below the melting point. The concept of "activation energy" represented by E^* in the Arrhenius equation was thus replaced by a combination of the parameters B and T_0 , the physical significance of which depended to some extent on which theory (e.g., Cohen-Turnbull, Adam-Gibbs) was employed to justify the functional relationship. More recently there has been some return to the activation energy concept, stimulated in part by experimental evidence that the Arrhenius equation begins again to give an accurate description of data taken on supercooled liquids at temperatures near to T_0 (27), and partly by the realization that the new equation was of little value in representing the temperature dependence of mobility in most molten salts. The simple reason for the latter situation is that hardly any pure salts (and relatively few salt mixtures) can readily be supercooled in amounts large enough to permit measurements of conductance or diffusion. Evidence that the conductivity of a number of salts may actually acquire a negative temperature coefficient at sufficiently high temperatures (28) led to the further realization that in any event no one equation could be expected to hold over the entire temperature range now accessible to the experimenter.

Studies of the simultaneous dependence of mobility on temperature and pressure have provided some new numbers with which to "play around" - "constant volume activation energies" and "activation volumes" (29, 30), but a coherent picture of their fundamental usefulness in understanding mechanistic details has yet to emerge. It is clear, however, that the systems studies exhibit some systematic trends, so that this may be a promising area for future study.

"Molten salt" character of fused hydrates. The difficulty of finding pure salts whose transport properties can be studied in a supercooled region was mentioned in the foregoing. Angell made a possible breakthrough in this area when he pointed out that a number of salt hydrates like $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ have melting points not much above room temperature and can readily be supercooled. He suggested that these may be considered as "pure fused salts" consisting entirely of hydrated cations and free anions (31).

Braunstein has recently reviewed experimental evidence for Angell's viewpoint (32). This consists generally of thermodynamic and structural studies. With respect to ionic transport, however, the "fused salt" nature of such hydrates seems to have been taken for granted by those exploring conductance, viscosity, chronopotentiometry, etc. in molten $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and related hydrates (33). For such studies to provide valid information relevant to ion mobility in molten salts, however, it is of primary importance to establish the reliability of the assumption that the tetrahydrated Ca^{+2} ion

moves as a single unit during electrolytic transport. This can be ascertained by carrying out a conventional Hittorf transference experiment. If the water molecules move along with Ca^{+2} , the "transport number" of the latter species relative to H_2O should be zero. During the past year attempts at direct measurement of this quantity were undertaken as part of this program. It is difficult to obtain high precision in these experiments, due to complications introduced by the electrode reactions. Results thus far of determinations carried out at 60°C are consistent with hydrated-ion hypothesis, but not sufficiently accurate to warrant an unequivocal conclusion. With a water excess amounting to 10 molecules per Ca^{+2} ion t_+ (relative to water) was found equal to about 0.2. It appears to drop rather abruptly as the $\text{H}_2\text{O}/\text{Ca}^{+2}$ ratio is decreased, its value at the critical 4:1 ratio being 0.00 ± 0.06 (based on 4 determinations). Further refinement of these data is needed.

In the meantime a number of ordinary diffusion measurements on the system $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ have been carried out. If the hydrated ion $\text{Ca}(\text{H}_2\text{O})_4^{+2}$ moves as a single entity in transport phenomena, the diffusion rate of H_2O should fall off rapidly as the ratio of H_2O to $\text{Ca}(\text{NO}_3)_2$ in the bath is reduced to four, after which values of D should be much less concentration-dependent, reflecting inter-diffusion rates of $\text{Ca}(\text{H}_2\text{O})_4^{+2}$ and $\text{Ca}(\text{H}_2\text{O})_3^{+2}$ (or some similar hydrated cation).

The experimental method involved following the change in weight of a frit containing a solution of one composition suspended in a large quantity consisting of the same components (salt and water) at some different composition. Diffusion runs were calibrated by first

carrying out the corresponding experiment in an aqueous electrolyte whose diffusion coefficient is well-known. Highly porous nickel "Feltmetal" was used as the frit material.

Since the method involved extensive calculations to obtain a proper analytical fit of experimental data to the theoretical equation, computer programs were developed to carry out this portion of the work. For a series of experiments in which the bath consisted of pure $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, good reproducibility was obtained, the limiting value of D at 70°C being $(2.76 \pm 0.11) \times 10^{-6} \text{ cm}^2/\text{sec}$ regardless of the initial composition in the frit. Additional experiments revealed the anticipated strong dependence of D on concentration in bath solutions containing more than $4\text{H}_2\text{O}/\text{Ca}^{+2}$.

The strong concentration dependence of D in the system $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} - \text{H}_2\text{O}$ provided an opportunity to examine quantitatively the effect of such behavior on the shape of the $(w_t - w_\infty)$ vs. t curve obtained when the suspended frit method is employed in such systems. Experimental data were fit to a variety of functional relationships, computing in each case the ability of the resulting equation to represent the data. The greatest accuracy was obtained by equating $w_t - w_\infty$ to a sum of two exponential time functions containing a total of four adjustable parameters. After suitable calibration, such a representation made it possible under certain conditions to evaluate the limiting slope, even when it was not feasible to prolong the run until this value was reached.

Analysis of the general applicability of the suspended-frit method for determining accurate diffusion coefficients nevertheless revealed severe limitations not pointed out in previous literature

reports. For example, significant variations in the effective pore length within a particular frit affect both the shape of the $\ln|w_t - w_\infty|$ vs. t curve, and the time required to reach the linear region from which D is generally calculated.

The most significant result of this study was the observation of a discontinuity in the plot of D vs. concentration at the stoichiometric composition $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. This was interpreted as evidence that one of the diffusing species must have the empirical formula $\text{Ca}(\text{H}_2\text{O})_4^{+2}$, while the nature of the opposing flux is determined by the excess or deficiency of water molecules at the particular concentration initially present in the frit. The result thus lends support to the view that $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ can be regarded as a "pure molten salt" with respect to transport as well as equilibrium properties.

IV. Significance of External Mobilities. Attention is directed once more to the evidence cited for correlation between experimental values of external mobilities in pure molten salts and theoretically-based electrical mobilities calculated from the values found for D_+ , D_- and Λ in the same systems. Such a correlation was implicit in the considerable degree of agreement among the corresponding transport numbers listed in Table I. The possible influence on $t_{+}(\text{ext})$ of the reference material was not discussed at that time.

Double-layer effects on external transport numbers. The apparent agreement among experimental values of external transport numbers obtained for particular salts using different reference materials appeared for a number of years to support the view that such quantities can be considered unique properties of the salts being studied. Since it is only through the electrical double layer that a molten salt can

interact with an external solid, an alternative explanation has prevailed in this laboratory: agreement of external transport numbers obtained with different reference materials has been attributed to similarity in structure and composition of the various interfaces involved. Experiments intended to confirm this hypothesis were eventually carried out employing salts whose transport numbers relative to commonly used reference materials had been well established in the literature. They showed that significantly different values could be obtained in PbCl_2 , PbBr_2 , and NaNO_3 by (a) changing the state of charge of the double layer using an external electrical potential, and (b) changing its structure and composition using very different reference materials. These results are shown in Tables III, IV and V.

TABLE III

External Transport Numbers of PbCl_2 and PbBr_2
with Varying Frit Parameters

Frit	PbCl_2		PbBr_2	
	t_- at 565°	No. of runs	t_- at 550°	No. of runs
UF Pyrex				
No external pot.	0.769 ± 0.024	69	0.668 ± 0.026	9
-5 volts	0.802 ± 0.037	9	0.725 ± 0.022	6
-10	0.858 ± 0.040	10	0.762 ± 0.035	6
+5	0.716 ± 0.037	7	0.646 ± 0.038	5
+10	0.760 ± 0.034	8	0.601 ± 0.026	4
F Pyrex	0.751 ± 0.018	19		
Selas Porcelain [†]			0.680 ± 0.012	
BN	0.852 ± 0.046	18		
Platinized UF Pyrex	+ 0.62 to -0.10	12		

[†]Runs carried out in "bubble cell".

TABLE IV

Dependence of t_{Br^-} in PbBr_2 on
External Reference Material

t_{Br^-} and Std. Dev.			
Temperature	Pyrex Frits (Grades UF and M)	Selas Porcelain	Boron Nitride (Grade A)
448°C	0.643 ± 0.008	0.650 ± 0.013	0.730 ± 0.018
495	0.651 ± 0.006	0.661 ± 0.010	0.782 ± 0.006
514	0.654 ± 0.005	0.666 ± 0.009	0.756 ± 0.014

The demonstration of such "double-layer-effects" on external transport numbers appeared to fulfill satisfactorily a primary objective of this program. Although an explanation of the observed sign and magnitude of each variation might be considered desirable in elucidating more fully the significance of these measurements, such an excursion into the realm of surface chemistry could present formidable problems unrelated to present goals. Further analysis in this research program was, however, deemed to be justified insofar as it concerned the relevance of such measurements to understanding the significance of external mobilities.

TABLE V

External Transport Numbers in Molten NaNO_3 at 350°

Separator (or support) material	Method	t_{Na^+} and std. dev.	Ref
Pyrex	Vol. change	0.71 ± 0.01	(34)
Pyrex	Tracer	0.68 ± 0.02	(35)
Pyrex	$(dh/dt)_{t=0}$	0.702 ± 0.015	(36)
Alumina	"	0.719 ± 0.002	"
Porcelain	"	0.745 ± 0.018	"
Electrokorund	Tracer	0.72 ± 0.03	(37)
(Glass fiber paper)	λ_+/Λ	0.690 ± 0.013	(38)
(Quartz fiber paper)	"	0.701 ± 0.021	(39)
(Alumina fiber paper)	"	0.710 ± 0.016	(40)
(Asbestos paper)	$\ell_+ / (\ell_+ + \ell_-)$	0.69 ± 0.02	(41)
Boron nitride	$(dh/dt)_{t=0}$	0.607 ± 0.010	This work (42)
Stainless steel	"	0.779 ± 0.028	"

In this regard one may still raise the following question: If different values of the transport numbers of a particular salt are found for different reference materials, is it possible to justify selecting any one value as being more "valid", (i.e., relevant to ionic transport in the bulk liquid) than the others? If the answer is negative, it is not possible to justify further measuring and reporting of external transport numbers, except as the results may contribute to an understanding of the interaction of molten salts with specific solid surfaces, or perhaps to some practical application.

The situation may not be so clear-cut, however, if the use of different separator materials involves considerable variations in pore size. The possible importance of pore size may be demonstrated by considering the measurement of liquid viscosity using a capillary viscometer. Here the (external) capillary serves as reference in determining a transport property ascribed to the bulk liquid. In relating volume flow to viscosity, however, it is assumed that the liquid at the solid-liquid interface is stationary. Velocity increases with distance from wall, so that the flow rate is determined by the shearing of successive liquid "layers", most of which are far from the interfacial region. Thus, the properties of the reference material are irrelevant. If, however, the capillary radius is sufficiently small, a substantial fraction of the liquid it contains may have "surface" properties different from the bulk. The apparent "viscosity" is then found dependent on the nature of the capillary material.

The possibility outlined above must be considered when porous materials are used as external references, whether in viscosity or transference measurements. In the latter case, however, ionic velocities reach limiting values within a few ionic diameters of the wall, so that their magnitudes relative to that wall are determined in the double-layer region. Recognition of this fact formed the basis for the postulate that external transport numbers should depend on the nature of the reference material. Nevertheless it should be apparent that the values found with a particular material are expected to be independent of pore size, provided this diameter is large compared with the double-layer "thickness". At the other extreme, obtaining a substantial contribution to the total ionic transport from migration through pores with dimensions comparable to ionic diameters would be analogous to using an "ionic sieve". A porous material in which this occurred could not validly be used to test the hypothesis that external transport numbers are properties of the bulk salt alone, any more than such a material could be used in flow-rate experiments to determine viscosity values consistent with those found using relatively large capillaries. Before concluding that the tabulated results provide adequate justification for asserting that any externally determined transport numbers are properties of the salt-reference interface involved, it is necessary to examine the possibility that pore diameters in the materials employed were too small to permit valid comparisons.

Pore sizes of reference materials. Only the "maximum pore diameter" is specified by the manufacturer for each grade of Pyrex frit. A method was developed, therefore, by which a mean value can be com-

puted from a combination of the observed electrical resistance and the "time constant" which is a measure of the resistance to bulk flow of the salt through the frit. This method will be described in the following section. In the case of Pyrex frits it showed that the mean pore diameters are of the same order of magnitude as the stated maxima. Since the smallest of these is around 1 micron, which is thousands of times larger than ionic diameters, the assertion that most of the salt inside the frit has the properties of the bulk liquid is certainly warranted. Thus, it is not surprising that results obtained with different grades have shown good agreement. The demonstration that application of a 5 or 10-volt potential to an externally wound platinum wire produces systematic variations in the transport numbers found for molten PbCl_2 and PbBr_2 relative to Pyrex frits (Table III) therefore appeared to establish unequivocally the role of the double layer in determining external transport numbers.

However, subsequent attempts to explore further the effects of such externally applied potentials failed to reproduce the earlier observations. Transport number measurements on both PbCl_2 and PbBr_2 employing Pyrex frits wound externally with Pt wire yielded only the zero-voltage values for applied potentials as large as ± 36 volts. As yet this discrepancy is unaccounted for. The initial experiments were done with considerable care, and a number of internal checks for consistency seem to substantiate their validity. Since comparable or greater care was exercised in obtaining contrary results, however, it cannot be asserted that the existence of transport number variations in Pyrex frits caused by externally imposed voltage variations has been established unambiguously in our laboratories.

Remaining evidence for a double-layer effect consists of observed variations in the transport numbers of PbCl_2 , PbBr_2 , and NaNO_3 associated with the use of different reference materials. Thus, although previous work had shown the values to be unaffected (within experimental error) by changing from Pyrex glass to other refractory oxide materials, more drastic changes (to boron nitride and to stainless steel) gave significantly different results in each salt tested (Tables III, IV, and V). They appear to demonstrate unequivocally a genuine double-layer "effect". Unfortunately, however, information regarding pore dimensions in these materials is insufficient to rule out the possibility that a significant fraction of the salt inside some of the separators employed is contained in pores of such high surface-to-volume ratio that it can no longer be considered to have the properties of the bulk liquid. The flow rate and electrical resistance obtained at the time of the transference experiments was only adequate to assign upper limits to the average pore diameters. Calculations indicated smaller values than in any of the Pyrex frits, but not necessarily too small. The reinvestigation of previous external transference number results thus indicated the importance of adequate pore characterization accompanying any future use of new porous reference materials.

Characterization of porous materials in electrolytic media.

The importance of pore-size information in interpreting the significance of external transport numbers was discussed above. A variety of experimental techniques exist that purport to measure pore-size distribution or related quantities (like the total internal surface area of a frit). Results of such experiments may not be applicable,

however, when they involve interaction of the porous material with mercury, nitrogen, or other fluids with properties very different from the molten salts being studied. An effort was therefore undertaken to identify the pore properties "seen" by the electrolyte itself, to be accomplished by confining experimental measurements to phenomena involving only the interactions of interest. Two measurements that can readily be carried out with only molten salt in the pores of the frit are electrical resistance and flow-rate determinations. The following simple analysis can then be applied to the results.

The frit is regarded as a bundle of parallel capillaries, each of diameter D_p . For this model Ohm's and Poiseuille's laws can be combined to give the relation

$$D_p = 4r \sqrt{\pi \kappa \eta a R / \rho g}$$

Here r is the radius of each vertical tube in which the relative rates of level change are observed during a determination of the "time constant" a for flow of the salt through the frit; R is the electrical resistance determined across the frit; κ is the specific conductivity of the salt; η its viscosity, and ρ its density; g being the gravitational constant. In studies of UF Pyrex frits containing molten $PbCl_2$, values of D_p ranging from 0.6 to 1.6 μ were calculated from this equation, showing that although there is considerable variation among individual frits, most of the "pores" are of the same order of magnitude as the nominal "maximum pore diameter" of 0.9 to 1.4 μ reported by the manufacturer. A comparison of observed t_a with corresponding D_p values for the various frits employed is shown in Table VI. These results show that the slight decrease in t_a with

increasing "maximum pore diameter" not ruled out by earlier measurements (43) was the result of experimental uncertainty; conversely, they demonstrate unequivocally the independence of t_e on effective pore diameter in Pyrex frits.

TABLE VI
Chloride Ion Transport Number for $PbCl_2$ at 575°
in Frits of Differing Effective Pore Diameters.

<u>Number of Runs</u>	<u>D_p (microns)</u>	<u>t_e and std. dev.</u>
5	0.6 - 1.0	$0.772 \pm .023$
7	1.2 - 1.3	$0.781 \pm .015$
25	1.4 - 1.6	$0.780 \pm .013$

Now it is possible to perform still another measurement, a determination of apparent porosity P , the result of which depends on the pore volume filled by the electrolyte. This quantity can be combined with the experimental R to obtain an expression for l_p , the average pore length:

$$l_p = \pi \bar{D}_f^2 \tau R P / 4$$

where $\bar{D}_f$ is the frit diameter. The calculated value of l_p can then be compared with l_f , the directly measurable thickness of the separator. Since the "pores" are irregular channels extending from one side of the separator to the other, l_p is expected to exceed l_f by a factor τ ("tortuosity factor") in the range 1.2 to 1.8. Any large discrepancy from this range would be indicative of some fundamental inconsistency in the model (provided all the data employed were reliable).

Knowledge of the porosity also makes it possible to determine N_p , the total number of pores in the frit,

$$N_p = P(D_f/D_p)^2$$

after the mean pore diameter D_p has been obtained.

An experimental test of the utility of these relations was initiated with some measurements in which aqueous electrolytes were used to characterize different grades of Pyrex frits (F, UF, and UF). As indicated earlier, only the maximum pore diameters are specified by the manufacturer, these being based on an ASTM test in which one determines the minimum pressure required to force an air bubble through a frit filled with water. The initial objective was to ascertain whether "reasonable" values of the parameters D_p , N_p , and τ are obtained, and whether these are independent of the properties of the electrolyte employed (nature of salt, concentration, temperature).

Preliminary results of flow-rate and resistance measurements have shown good agreement among the values of D_p obtained for any given frit using different electrolytes (KCl, LiCl and HCl), each at two quite different concentrations, e.g., 4 m and 0.5 m. Although D_p is generally found to be of the same order of magnitude as the nominal "maximum pore diameter", considerable variations have been observed among different frits of the same grade. It is therefore necessary to characterize each frit individually before using it in subsequent experiments.

V. Simple Binary Mixtures. Under this heading will be considered only mixtures of two salts having one ionic species in common. Little if any work has been done on ion mobility in more complicated mixtures, nor do efforts in that direction appear warranted at this time by our present level of understanding.

The study of simple mixtures permits observation of the effects of continuous variations of composition on the mobilities of individual species. It also introduces the possibility of comparing such effects with the corresponding thermodynamic behavior of the system being studied. Significant correlations between ionic mobility and the thermodynamic behavior of electrolytic solutions are well known. The $\sqrt{c}$ dependence of both Λ and $\ln \gamma_{\pm}$ in dilute aqueous solutions was discovered long before the Debye-Huckel-Onsager theory provided a unifying basis of understanding. Thus it may be hoped that analogous discoveries in molten salt mixtures can point the way to useful theoretical developments.

Thermodynamically, many binary salt mixtures are not far from "ideal" in their properties. Some deviation from ideality is almost always found, however, and it is possible to state some generalizations about such deviations. The most nearly ideal systems that have been studied extensively are mixtures involving two different alkali metal cations and either nitrate or a halide as the anion. In such systems the enthalpies of mixing are almost invariably negative (exothermic), while there is almost no observable excess entropy of mixing. The magnitudes of the enthalpy changes can be correlated with the sizes of the ions involved, and some very useful generalizations in this respect have been made by Kleppa and his coworkers (44).

Relevant theoretical developments have been extensive, the more recent developments having been reviewed by Angell (1). Rather than attempt a critical discussion here, it will simply be pointed out that in addition to simple coulombic effects there is good evidence for the importance of polarization of the large anions in the unsymmetrical field presented by mixing of different-sized cations, and of short-range van der Waals repulsions between anions. The former contributes negatively to the heat of mixing (45), while the contribution from the latter is expected to be positive (46).

In binary systems other than those mentioned above, deviations from ideality may be considerably greater. Such behavior has often been attributed to the formation of "complex ions", but the use of this single concept does not appear consistent in describing such extreme examples as AlCl_4^- (unambiguous) and the sometimes postulated species MgCl_3^- . Covalency of chemical bonding would be expected to have an effect on thermodynamic properties, but it is not clear to what extent the latter can be used to draw inferences about the former. This is one area in which suitable transport studies may eventually be of some value, although it must be admitted that in a number of instances examination of conductivity isotherm has lead investigators to conclusions about structural entities not supported by other types of information.

Dependence of diffusion mobilities on composition. Systematic determinations of ionic self-diffusion coefficients in binary mixtures have been carried out in the laboratories of Chemla (Paris) and Ketelaar (Amsterdam). Alkali nitrate mixtures were studied in both places with generally good agreement of results, and more re-

cently Chemla, Lantelme, and Mehta have completed a study of the KBr-LiBr system (47). In the nitrate systems the general tendency is for the diffusion mobilities of both cations to vary monotonously from a lower limit in the salt whose "proper" cation has the smaller D_+ to an upper limit in the other salt. Thus, in the system $\text{KNO}_3\text{-NaNO}_3$, Lantelme and Chemla found that the ratio $D_{\text{K}}/D_{\text{Na}}$ remained constant at 0.84 ± 0.02 over the entire range of composition at three different temperatures (48). The halide system was not markedly different: the mobilities of both Li^+ and K^+ rise continuously from their values at the KBr end of the range, that of Li^+ always remaining larger than that of K^+ . These results seem rather uninteresting until one reconsiders them in the light of the behavior of electrical mobilities in the same systems (to be described below).

In binary mixtures at least two types of diffusion coefficients other than the self- or tracer-diffusion coefficient (to which all preceding discussion of diffusion mobilities has been confined) can be defined. The "ionic diffusion coefficient" obtained in chronopotentiometry is referred to in the present work as the "chronopotentiometric diffusion coefficient" D_{ch} . It was shown by a rigorous ineversible thermodynamic treatment that D_{ch} could be related to the "ordinary (or mutual) diffusion coefficient" D_{ij} , obtained by interdiffusing different concentrations of the two salts, and the "internal transport number" θ_{ik} (or t_{ik}) which is the fraction of current carried by one of the two like-charged species during electrolysis when the oppositely-charged species is taken as reference (9). Both of these additional types of diffusion coefficients have been the subject of experimental studies in this program.

The measurement of ordinary diffusion coefficients by the diaphragm cell technique was adapted to fused salt mixtures and applied to the system $\text{AgNO}_3\text{-NaNO}_3$ (49). By extrapolation of the data at a series of low concentrations the infinite dilution value of the diffusion coefficient of Ag^+ was found to equal $(1.96 \pm 0.08) \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at a temperature of 310°C . This was the approximate figure to be expected on the basis of other considerations, and demonstrated the extreme inaccuracy of the only results for ordinary diffusion coefficients in binary fused salts previously reported in the literature (50).

Of perhaps greater interest are the chronopotentiometric studies undertaken as a part of this program. The phenomenological analysis mentioned above showed that in the very dilute solutions normally employed in chronopotentiometry D_{ch} is substantially identical with both ordinary and self-diffusion coefficients of the ion being studied. The theoretical analysis was completed with the development of a new method for taking account of double-layer charging current in interpreting the results of chronopotentiograms. Previous authors had used a basically empirical approach, apparently failing to realize that the slope of the chronopotentiometric "wave" gives a direct indication of the charging current at any point on the curve. A subsequent verification of this approach by Olmstead and Nicholson lead them to the conclusion that the methods of Delahay and of Reinmuth were inadequate, and that "the method of Laity and McIntyre... should be adopted for all experimental transition time measurements" (51, italics theirs).

Precision apparatus for the determination of chronopotentiometric diffusion coefficients in molten salts was then developed. Application to the system $\text{AgNO}_3\text{-NaNO}_3$ at very low concentrations of Ag^+ yielded results in excellent agreement with the figure obtained by the diaphragm-cell method. Here, however, it was possible to extend the measurements to substantially higher temperatures, and a set of results of comparatively high precision (better than $\pm 2\%$) were obtained at 315, 340, and 360°C.

The effect of continuously changing composition on diffusion mobilities of the cations in the system $\text{KNO}_3\text{-NaNO}_3$ has been described in the foregoing. Employing this system as a "solvent", the effect of its composition on the mobility of Ag^+ was observed by carrying out chronopotentiometric measurements on dilute solutions of silver ion over the entire range of solvent composition (52). The mobility of this "solute" ion was found to be greater than either of the solvent cations, and to decrease with increasing potassium nitrate concentration at a rate exactly equal to the decrease that had been observed in the self-diffusion mobilities of the two solvent cations (48). However, the effect of temperature on the mobilities of the latter ions was greater than the effect observed on that of silver. These results showed that the simple model employed in deriving the Stokes-Einstein equation may appear valid for the solvent cations, but is not strictly applicable to the mobilities of solute ions in this system.

The study of the effect of solvent on the mobility of a solute cation (silver) was extended to examination of the effects on diffusion mobility of changing both cation and anion in the pure

alkali halides (52). Solvents for which successful results were obtained included the following: sodium chloride, potassium chloride, sodium bromide, potassium bromide. Comparing results at the same temperature (810°C) it was observed that silver ion is most mobile in sodium bromide and least mobile in potassium bromide. A somewhat smaller decrease is observed in going from sodium to potassium chloride. This effect of changing cation size will be seen to be exactly what would be predicted from the model used to explain the electrical mobility results to be described in the next section. The effect of anion size, while not systematic, will be seen to provide an even stronger argument for the same model.

Dependence of electrical mobilities on composition. Particular importance was attached to this area in the initial undertaking of this program, since it provided the only clear-cut method of comparing relative electrical mobilities of ions in molten salts. In view of the ambiguous significance of external mobilities, and of the trivial nature of internal mobilities in pure salts, it is only by comparing internal mobilities of like-charged species present together in the same melt that unambiguous conclusions can be drawn as to which is the more mobile species.

To obtain such information for a mixture with two different cation species, two types of experimental measurements are required: equivalent conductance of the mixture and a transference number determination in which the anion serves as reference. Although many conductivity isotherms of binary mixtures had been reported in the literature, transference results at the time this program was initiated were inadequate to provide any basis for generalization. The

situation was rectified considerably by the results obtained for relative cation mobilities in the system KCl-LiCl (53).

First, a series of conductance measurements was aimed at establishing reliability of the figures over the entire range of concentration and a significant temperature range. Results were again in good agreement with the work of Van Artsdalen and Yaffe, thereby establishing that some Russian results previously reported for this system were in error. A small discrepancy with the Van Artsdalen figures at the LiCl end of the range was confirmed by Duke and Bissell (17). Additional data taken for the first time at concentrations very near the ends of the isotherms showed that some workers' speculations about the likelihood of unusual behavior in these regions were not in accord with experimental fact.

A modified Hittorf technique for determining relative transference numbers of like-charged ions was then applied to the system. Substantially the whole range of concentration and a significant range of temperature were examined. Results showed a strong dependence on concentration for the mobilities of both cations, that of Li^+ being especially sensitive to addition of K^+ . The resulting mobility decrease is so great that K^+ actually becomes the more mobile ion at concentrations greater than about 25 mole percent. Indeed, the extremely low mobility of Li^+ in solutions rich in KCl was shown to account for the previously puzzling minimum in the isotherm of equivalent conductance. A simple model was shown to account qualitatively for these results. It was essentially the anion-polarization model proposed by Lumsden to account for the exothermic heats of mixing commonly observed in such systems (45). This suggested

that the observed mobility variations were a result of the change in cation-anion interactions effected by changing the polarizing power of a neighboring cation. The model could also be used to explain negative deviations from additivity of viscosity in such systems (an observation that was contrary to Walden's rule), and predicted a somewhat smaller dependence on composition of diffusion mobilities, an observation that has now been verified, as previously noted.

The behavior of relative cation mobilities in KCl-LiCl has subsequently been shown to be quite general for mixtures involving two alkali metal cations. Thus, similar behavior has been reported for KBr-LiBr (47) and for a number of alkali nitrate pairs (54, 55, 56, 57 and other papers by the same authors).

As indicated earlier, all of the alkali-alkali systems mix exothermically, and hence show thermodynamic behavior consistent with the anion-polarization model. There are systems, however, for which ΔH_{mix} has a positive sign. In the present program an effort has been under way to ascertain the behavior of relative ion mobilities in such systems. A particularly interesting class of systems in this respect consists of mixtures of silver bromide with the alkali bromides. Heats of mixing were found by Hildebrand and Sals-trom to be negative when the alkali cation is larger than silver, and positive when it is smaller (58). The behavior is systematic and fits nicely into the category of "regular solutions" as defined by Hildebrand.

The first stage of this work consisted of conductivity (and density) determinations in the systems AgBr-KBr, AgBr-NaBr, and

AgBr-LiBr, the first being a "normal" (exothermic) system, the other two endothermic. The equivalent conductance isotherms for AgBr-KBr showed the expected negative deviation from additivity, including a distinct minimum similar to that found in LiCl-KCl. Transference experiments confirmed the similarity in terms of the individual ion mobilities (59). Conductivity isotherms for AgBr-NaBr and AgBr-LiBr were surprisingly similar to those for AgBr-KBr, the deviation from additivity being negative in all cases and smallest for AgBr-NaBr. This does not exclude a different behavior of the individual mobilities. The transference experiments conducted thus far have been inconclusive due to experimental difficulties, but seem to indicate that the concentration dependence of mobility in AgBr-LiBr and AgBr-NaBr may indeed be distinctly different from the cases already elaborated. For both systems it appears that the ion mobilities may pass through minima, rather than change monotonously with concentration as has been observed in the previous cases. There is even some evidence that the mobility of silver ion in dilute solutions of these alkali bromides may be greater than that of the solvent cation. If this is the case, it is indeed a different behavior from other systems that have been studied, and indicates the possibility of additional correlations between ion mobility and thermodynamic behavior.

Concentration cells with transference. As part of the present program a rigorous treatment of electromotive force in cells containing liquid-liquid and liquid-solid interfaces was developed from the thermodynamics of irreversible processes (60). This showed how the emf's of such cells depend on the same internal transference

numbers that were used in obtaining the relative ion mobilities described in the preceding section. Conversely, measurements of emf can be used to obtain the relative transference numbers needed in determining internal mobilities. As in aqueous solutions, however, the emf method is not as accurate as the D. C. methods. Some emf measurements were carried out in this program, nevertheless, after it was found that the transference results described above for the AgBr-KBr system differed quite substantially from the conclusions to be inferred from emf measurements on concentration cells reported by Murgulescu and Sternberg (61). According to these workers' results, the mobilities of Ag^+ and K^+ should have been found equal at all concentrations. It was therefore decided to repeat some of their measurements. New emf results were entirely consistent with the relative mobilities that had been found in the direct transference measurements, and gave no support to the claim of equal cation mobilities (59).

An as yet unresolved discrepancy exists in the relative cation mobilities of the system LiCl-PbCl_2 as determined by moving boundary experiments (62) and by emf measurements (63). Both results are in good agreement at concentrations from pure LiCl to about 80 mole % PbCl_2 , indicating a monotonous and roughly parallel decline of both cation mobilities. This same trend appears to continue in the emf results, but the moving boundary experiments indicate a sudden and steep rise in the Li^+ mobility as its concentration becomes more dilute.

Significant discrepancies also exist in the relative anion

mobilities in the system $\text{AgNO}_3\text{-AgCl}$ on the basis of direct transference and emf measurements. Two direct transference studies gave widely divergent results (64, 65) while some concentration cell data (66) and some recent determinations of "gravitational emf" (67) only serve to confuse the issue still further. If the last-mentioned results are correct, it appears there may be a cross-over of anion mobilities with changing composition, just as has already been noted for cation mobilities.

Dependence of mass effect on composition. In the discussion of the mass dependence of internal electrical mobilities in pure salts it was pointed out that the magnitude of the mass-effect μ_i generally lies between -0.01 and -0.2. Only two measurements of this effect in mixtures have been reported, and both gave somewhat surprising results. A single determination (68) performed on a mixture consisting of 97.8 mole % LiCl and 2.2 mole % KCl yielded a value for μ_K of -0.32. Furthermore, a study of the composition dependence of μ_{Li} in the system LiCl-PbCl_2 (52) indicated values in the "normal" range from pure LiCl down to about 30 equivalent % LiCl , below which this mass effect rapidly became much larger, reaching -0.3 at 10% LiCl . These observations have been interpreted as further evidence for a "coupling" mechanism in the transport of similar cations. Such coupling is presumably no longer possible when the species being studied becomes sufficiently dilute (24).

Dependence of mobility on temperature. This review will conclude with two observations concerning temperature effects that pertain particularly to the study of mixtures. The first concerns the behavior of "activation energies" of ionic mobility as a function of composition.

In the study of relative cation mobilities in the system AgBr-KBr it was possible to obtain separate temperature dependences for the mobility of each species (59). The activation energies calculated from these results were found to decrease with decreasing concentration of AgBr for both ions. The interesting point about this result is that precisely the opposite conclusion might have been drawn from an examination of the temperature dependence of Λ for the mixture. The latter quantity rises with decreasing AgBr content due to the increasing contribution of the mobility of K^+ , the ion with the higher activation energy of the two.

The preceding observation emphasizes the pitfalls of attempts to draw conclusions about the characteristics of electrical mobilities in binary mixtures from an examination of the behavior of Λ without ascertaining the individual ionic contributions of which Λ is composed. This may have significant implications for the last observation to be made here concerning temperature dependence.

The potential value of studying supercooled melts as pointed out by Angell and coworkers was mentioned in the discussion of pure salts, where it was pointed out that hardly any pure salts can be supercooled in quantities large enough for experimental studies of ionic mobility. Thus, most of the experimental work pertaining to ion mobility in supercooled melts has been carried out on mixtures, such as certain intermediate compositions of the system $Ca(NO_3)_2-KNO_3$ (69). Examinations of the concentration and temperature dependence of Λ in such systems have led to a number of interesting generalizations. In none of these systems, however, have the values of Λ been dissected into their ionic components by suit-

able transference experiments.

VI. References

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Reports and Publications

A. Printed Articles

1. R. W. Laity and C.-A. Sjöblom, "Double-Layer Effect on 'External Transport Numbers' in Molten Lead Chloride," J. Phys. Chem., 71, 4157 (1967).
2. R. W. Laity and A. S. Tenney, "Relative Cation Mobilities in Silver Bromide-Potassium Bromide Melts," J. Phys. Chem., 74, 3112 (1970).

Additional articles still in preparation include papers based on the following reports to AEC: NYO-3608-6, 9, and 12. There will also be a publication entitled "Diffusion in Calcium Nitrate-Water Mixtures" by R. W. Laity and Z. F. Mathe, and (probably) one on "Possible Effect of Porous Separators on Internal Mobilities in Molten Salt Mixtures" by R. W. Laity and S. J. Heron.

B. Ph.D. Theses

1. A. S. Tenney, "Irreversible Processes in Ionic Melts." Rutgers University (1971).
2. Z. F. Mathe "Some Transport Studies in Liquids." Rutgers University (1973). [Most of the experimental work reported in this dissertation was performed during the contract period and depended on AEC funds.]

C. Reports to AEC

1. Annual Progress Reports: NYO-3608-2,3,7,8,10
2. Specific Reports on Various Phases of the Program
NYO-3608-1 "Charged Porous-Plug Transference Numbers"
NYO-3608-4 "Relative Cation Mobilities in Molten Salt Mixtures"
NYO-3608-6 "Some Factors Affecting External Transport Numbers in Pure Molten Salts"
NYO-3608-9 "Effect of External Reference on Transport Numbers in Pure Molten Sodium Nitrate"
NYO-3608-12 "Effect of Various Parameters on Transport Numbers in Pure Lead Chloride"

D. Reports Presented at Meetings

1. "Ionic Transport in Binary Salt Mixtures." Presented by R. W. Laity at Gordon Research Conference on Molten Salts, Meriden, N. H., Sept. 1965.

2. "Effect of Externally Controlled Variables on External Transport Numbers in Pure Molten Salts." Presented by R. W. Laity at the National ACS Meeting in Miami, Fla., April, 1967.
3. (Same title as item 2 above). Presented by R. W. Laity at Gordon Research Conference on Molten Salts, Meriden, N. H., August, 1967. (Note: The author also served as Vice-Chairman of this Conference).
4. "Control of External Transport Numbers by Application of Applied Potentials to the Reference Material" by R. W. Laity and C.-A. Sjöblom. Presented at the EUCHEM Conference on Molten Salts, Pavia, Italy, May 1968.
5. "Double-Layer Effect on External Transport Numbers in Pure Salts: PbBr_2 and NaNO_3 ." Presented by R. W. Laity at the Gordon Research Conference on Molten Salts, Meriden, N. H., August 1969. (Note: The author also served as Chairman of this Conference).