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GLASS-MOLTEN SALT INTERACTIONS

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CONTENTS

I. Introduction.....	355
II. Constitution and Structure of Glass.....	356
III. Molten Salts.....	357
IV. Diffusion and Ion Exchange.....	357
A. Methods for Studying Diffusion.....	358
1. Weight Change.....	358
2. Diffusion Profiles.....	358
3. Spectrophotometry and Spectroscopy.....	359
4. Electrical Conductivity.....	359
5. Mechanical Deformation.....	359
B. Characteristics of Ionic Diffusion in Glass.....	359
1. Dependence of Diffusion on the Nature of the Salt.....	359
2. Effect of Glass Composition on Diffusion Rate.....	360
3. Effect of Melt Anion on Diffusion Rate.....	361
4. Effect of Temperature on Diffusion Rate.....	361
C. Theories of the Diffusion Mechanism.....	362
D. Diffusion and Conductance. The Nernst-Einstein Equation.....	363
1. Molten Salts.....	363
2. Glasses.....	363
E. Applications.....	364
V. Electrical Conductance.....	364
A. The Conduction Process.....	364
B. Mixed Glasses.....	365
VI. Electrolysis of Glass.....	366
VII. Electrochemical Potentials at Glass-Molten Salt Interfaces.....	367
VIII. Glass Membrane Reference Electrodes.....	369
A. Sodium-Glass Electrodes.....	369
B. Electrode Reactions not Involving Sodium.....	370
C. Glass Electrodes with Unknown Electrode Reactions.....	370
IX. Conclusions.....	371
X. References.....	371

I. INTRODUCTION

The electrical properties of glass have been studied ever since the days of Cavendish in the late 18th century. Work on molten salts began a century later with studies by Lorenz and co-workers (55). However, except for isolated papers, interest in this latter field did not revive until approximately 1950, with considerable growth since then.

Thus, early work on interactions between molten salts and glasses resulted almost entirely from the interest of glass scientists who wished to study the ionic properties of glasses and who used salts as a source of ions which might migrate into the glass.

Only recently have molten salt chemists become interested in glass, primarily in connection with reference

electrodes using membranes but also because glass is a common container material which reacts with at least some salts under some conditions.

Surprisingly, the glass-molten salt interface does not seem to have been much studied, although the abrupt transition from ionic fluid to dilute solution with a correspondingly great change in several properties, *e.g.*, viscosity and ionic mobility, might be of interest in itself.

The purpose of the present paper is to focus first on those aspects of glasses and molten salts which are particularly relevant to interactions between them. Since these interactions are controlled primarily by the glass properties, considerably more space is devoted to them, in particular to those involving ions, *i.e.*,

electrical conductivity and electrolysis. The kinds of transport phenomena observed and their mechanism, rather than experimental details and values for the many commercially available glasses, will be emphasized. Since most studies of molten salt-glass systems have used silicates, only these will be discussed. Only those properties important for ionic transport are treated. The reader is referred to several excellent works for more detailed information (25, 57, 62, 96, 97, 103).

When salts and glasses come in contact, ion exchange will usually occur across the interface. Various aspects of this diffusion process will be discussed and then applied to the development of electrical potentials at this phase boundary.

II. CONSTITUTION AND STRUCTURE OF GLASS

Since this subject has been reviewed in more or less detail (57a, 62, 80, 87, 103a), it will be discussed only very briefly, particularly as it pertains to silicate glasses.

After early discussions as to whether glass could be described as a collection of microcrystals connected by amorphous zones (103a), the random network theory of glass structure was proposed by Zachariasen (107). In this model the glass retains the essential geometrical features of the liquid from which it has formed, but has lost the mobility of its major constituents. Thus glass is an extended three-dimensional network lacking symmetry and long-range periodicity. The glass-forming Si^{4+} cations are surrounded by polyhedra of oxygen atoms. The latter are either bridging, *i.e.*, linking two polyhedra, or nonbridging, belonging to only one polyhedron (87). Cations of charge other than $4+$ may exist in holes between the oxygen polyhedra, their concentration depending on the glass composition. This view of the structure is consistent with the results of X-ray studies of glasses (102).

The question as to which substances, particularly oxides, are capable of forming glasses has been studied extensively (87, 103a) but is not discussed here.

None of the commercially made forms of fused silica (35, 105) has the exact formula SiO_2 . It may contain water in the form of $-\text{OH}$ groups if made by hydrolysis of silicon compounds or by melting quartz in an atmosphere containing water vapor. If quartz is melted in a reducing atmosphere it is deficient in oxide ions, *i.e.*, contains an excess of electrons. The reduced and oxidized forms differ with respect to transport properties. In addition, various types of defects from the ideal structure (104), such as sites of deficient or excess oxide density and distortions of the lattice, affect the measured properties of silica. A small concentration of mobile cations, such as Na^+ , Li^+ , and H^+ (29), is responsible for the electrical conductivity of fused silica, particularly at elevated temperatures.

The properties of alkali silicate glasses differ from those of pure fused silica not only because of the introduction of the alkali metal cations but because the structure is also modified by the introduction of extra oxide ions (104) since the concentration of nonbridging oxygens is increased. In addition the oxygens in the structure are polarized and hence the $\text{Si}-\text{O}-\text{Si}$ bonds weakened. Thus the nature of the added ion is also significant for determining the details of the structure. The glass is then an anionic polyelectrolyte, the negative charge of the silicate network being balanced by the relatively mobile cations.

When the glass contains more than one mobile cation, its properties can in general not be predicted in any simple way from those of the two single-cation glasses (50, 51). The conductance of mixed alkali glasses is discussed in section VA.

Implicit in the common description of glass as a supercooled liquid is the recognition that glass has no definite melting point, as crystals do. Nevertheless, there is a clearly discernible difference between glass at ambient temperatures and in high-temperature regions in which the viscosity does not differ greatly from ordinary molecular viscous fluids. Between these two regions kinetic parameters such as viscosity and conductance vary exponentially in $1/T$, the variation being generally described in terms of rate theory. However, an Arrhenius-type equation

$$\eta = A \exp(-E/RT) \quad (\text{Eq } 1)$$

here written for the viscosity η leads to different values of the activation energy E over different temperature ranges. Nevertheless, for many properties E changes near a temperature, usually called the transformation temperature, in which the viscosity is approximately 10^{13} poise. This temperature, T_g , has some of the properties of a critical temperature in that a "corresponding-states" treatment of glasses can be based on it (66). For example, $\log \eta$ vs. T_g/T curves for many glasses lie on the same curve. Many physical properties change their temperature coefficient near T_g , but frequently the change occurs over a temperature range called the transformation region. The region marks the dividing line between the brittle and highly viscous states of glass. Above this region the times required for reaching the equilibrium configuration are comparable to experimental times (seconds to hours); below it they are of the order of years (20, 39). Thus the structure of the glass depends not only on temperature but on the rate of cooling, since only with very slow cooling can the equilibrium configuration be reached. Structures frozen in at the higher temperatures persist virtually unchanged at the low temperatures. If a glass is used in a molten salt environment below T_g , it is conceivable that such structure-dependent parameters, and not only compo-

sition, will influence the transport properties of ions in the glass.

At high temperatures the presence of foreign ions catalyzes the formation of the thermodynamically more stable crystalline forms of silica (28). The nature of the ion determines the particular modification obtained. For example, at 850°, a temperature at which quartz is the stable form, the large ions Rb⁺ and Cs⁺ catalyze the crystallization of cristobalite, the only structure open enough to accommodate them, whereas K⁺ leads to tridymite, Na⁺ to tridymite and quartz, and Li⁺ to quartz only.

When a silicate glass is used in a molten salt environment, ions from the melt diffuse into the glass and devitrification progresses from the interface into the interior. Generally no visible change occurs as long as the temperature remains above T_g , but as the glass is cooled it becomes opaque and shatters. The effect of foreign ions on devitrification may be explicable in terms of the change in glass composition produced by diffusion of ions from the melt. Whether or not crystallization occurs in a particular case depends on kinetic, rather than thermodynamic, factors. Thus in fused silica which has been immersed in a molten salt for some time, the speed of crystallization may be much greater than in silica not so exposed, because the viscosity is lowered by the diffusion of cations into the glass. Consequently, as the glass is cooled the crystalline forms of silica which have different densities form and the glass cracks.

III. MOLTEN SALTS

Although research on molten salts goes back to the beginning of this century, it is only in the last 20 years that this field has become recognized as a discipline with its own special techniques. One evidence for its relative maturity is the recent appearance of two books, summarizing much of the available information (5, 94). In addition, more specialized material is available in a monograph (91). In view of this wealth of material only a very brief summary is given here.

The "field" of molten salts is largely concerned with the properties of inorganic salts, hydroxides, and oxides above their melting points. The unique feature of molten salts is that, in contrast to ordinary liquids and electrolytic solutions, they are essentially ionic fluids. The chief exceptions to this general description are those salts which in the liquid state are almost entirely molecular, such as the mercuric halides.

Properties of salts which have been, and are being, studied extensively are the thermodynamic ones, both for single and multicomponent systems and their structural interpretation in terms of the species in the liquid (*e.g.*, complex ions) and the interactions between them. X-Ray and neutron diffraction and spectroscopy have been important tools in elucidating these.

Transport properties such as electrical conductivity and diffusion have also received considerable attention. Finally, the ionic nature of the material and the absence of a diluting solvent has led to interesting electrochemical studies involving metal-molten salt interactions and electron exchange across this interface.

Since most salts melt at temperatures considerably above ambient, the silicate glasses are no longer the insulators they are at that temperature, but conduct current to some extent. Consequently, the salt-glass boundary is essentially that between a concentrated and a dilute electrolytic solution, with not all ions present on both sides of the interface. On the melt side the viscosity is low and ionic density is high, leading to relatively high transport parameters (conductance, diffusion) for this phase. In the glass the opposite condition prevails. It follows that any migration of ions across the interface is controlled primarily by the properties of the glass. For example, the negative silicate network largely prevents anions from entering, and the size of the openings and the charge of the diffusing ions determine which cations may enter.

IV. DIFFUSION AND ION EXCHANGE

Since diffusion of both molecules and ions in glass has recently been reviewed in some detail (22), only those aspects of diffusion related to molten salt-glass systems are discussed here.

When molten salts and glasses come into contact, cations from the melt may diffuse into the glass. If the glass initially contains mobile cations, these diffuse into the molten salt. Whether, and to what extent, such ion exchange occurs depends on whether the ions in the melt can be accommodated in the glass structure without severe distortions of the silicate network, and on whether the glass contains diffusible ions. Evidence to support the suggestion (68) that net diffusion from molten salts into glasses may occur above the softening point by movement into "holes" without exchange is largely lacking. One difficulty with this concept is that, unless net diffusion of cations is accompanied by anion diffusion, large potential differences due to charge separation would be set up at the melt-glass interface which would inhibit further diffusion. However, the diffusion of oxide or hydroxyl ions which are usually present as impurities in molten salts may keep the glass electrically neutral. Since no information on this kind of diffusion seems to be available yet, the process discussed in this section is understood to be ion exchange.

Most of the studies concentrate on events on the glass side of the melt-glass interface. This is natural since ionic diffusion in molten salts is so rapid that the rate-limiting processes occur in the glass. Some of the work cited in this section is done by applying small

quantities of radioactive tracers on the glass surface and measuring their diffusion in the glass. Although no molten salts are involved, the phenomena observed are similar. The nature of the ion-exchange process in these experiments has not yet been studied, however.

A. METHODS FOR STUDYING DIFFUSION

Schulze (75) was the first to study diffusion from a molten salt (AgNO_3) into a (sodium) glass quantitatively, although the occurrence of such diffusion had previously been reported (36). He developed several of the methods which are still used to study diffusion. In this section these methods are described.

1. Weight Change

For all cases except self-diffusion, the exchange of an ion in the glass for one in the melt will lead to a weight change in the glass and a composition change in the melt. Although the occurrence of these two phenomena provides proof for ion exchange, the nature of the exchanging ions and the exchange ratio must be known for a more detailed analysis. In his initial experiments Schulze (75) showed in two ways that this exchange is 1:1. In the first experiment, the weight increase of a sodium glass immersed in AgNO_3 was noted. The glass was then dissolved in HF and the silver in it determined analytically. The total weight change was found to be consistent with the hypothesis that for each silver ion which had diffused into the glass one sodium ion had diffused out. In the second experiment the weight change of the glass was compared with the sodium which had diffused into the AgNO_3 . The results of both experiments were consistent with 1:1 exchange within 10%.

Warburg (100) was the first to show that the diffusion constant D of an ion diffusing into glass could be determined from a knowledge of the weight change as a function of time by using Fick's law, and, from the result of the Schulze experiment, that the total number of ions in the glass is constant. If D is constant, Fick's second law for one-dimensional diffusion is

$$\frac{\partial C_2}{\partial t} = D \frac{\partial^2 C_2}{\partial x^2} \quad (\text{Eq 2})$$

where C_2 is the concentration of the ion diffusing in the x direction. Doremus has pointed out (22) that the mass of material diffusing into the glass is necessarily proportional to \sqrt{t} regardless of the functional relationship between D and concentration. Thus, without a knowledge of the diffusion profile, the calculated value of D corresponds to only one particular concentration. The linear relation between weight change and \sqrt{t} has been confirmed by several authors for a variety of ions (23, 38, 44, 49, 68, 78).

Doremus (23) has recently used a more sophisticated version of the weight change experiment to ob-

tain the diffusion constant of Ag^+ diffusing from AgNO_3 into a sodium glass. The total number of moles of silver, m_2 , which have diffused into the glass in time t is

$$m_2 = A \int_0^t J_2^0 dt = -2A \sqrt{\bar{D}^0 t} \left(\frac{\partial C_2}{\partial z} \right)_{z=0} \quad (\text{Eq 3})$$

where A is the area of glass in contact with molten salt, J_2^0 is the flux across the glass-melt interface ($x = 0$), \bar{D}^0 is the interdiffusion coefficient when $x = 0$, and $z = x/\sqrt{\bar{D}^0 t}$. m_2 is obtained by measuring the change in weight ΔW after diffusion.

$$m_2 = \frac{\Delta W}{M_{\text{Ag}} - M_{\text{Na}}} \quad (\text{Eq 4})$$

4% HF solution was used to etch off successive layers of glass, and the resulting solution was analyzed with radioactive silver tracer. The thickness d of the etched layer was calculated from the change in weight ΔW after etching using the equation

$$d = \frac{\Delta W - m_{\text{Ag}}(M_{\text{Ag}} - M_{\text{Na}})}{\rho_0 A} \quad (\text{Eq 5})$$

where m_{Ag} is the total number of moles of silver in the layer, M is the molecular weight, and ρ_0 is the density of the glass before diffusion.

2. Diffusion Profiles

The diffusion profile, *i.e.*, a concentration-distance ($c-x$) diagram, can be constructed by exposing the glass to the salt for a given length of time. After removal of the superficially adhering salt, the glass is etched with dilute HF to remove thin successive portions of the glass. From the weight change and the density of the glass, the thickness removed is determined and analysis of the HF solution gives the ionic composition of the removed layer. This method, first developed by Schulze (75), has more recently been used with radioactive tracers as the diffusing species. Doremus has used tracers with the HF technique (23), and Blau, Bristow, and Johnson (6, 40, 41) have worked out several techniques which use tracers for the determination of diffusion profiles. In the "grinding technique" layers are mechanically removed instead of etched; in the "photographic technique" the amount of tracer diffused into the flattened end of a cylindrical rod is determined by radioautography and a photodensitometer, a known thickness of rod being removed between exposures; in the "continuous sectioner" method the rod is converted into a continuous strip of glass powder by grinding on emery paper. In this way a 1-cm rod can be converted into a 25-cm strip on the paper, thus magnifying the diffusion zone enormously.

3. Spectrophotometry and Spectroscopy

When silver diffuses into a sodium glass the originally colorless glass gradually turns yellow and then brown. Thus the amount of silver can be determined spectrophotometrically (38).

Pask and Parmelee (68) used a quartz spectrograph to get a diffusion profile and also examined portions of the silver-containing glass spectrophotometrically. More recently Ito (38) has measured a concentration profile spectrophotometrically. The silver-containing glass exhibits an absorption peak at 314 μ , and the absorbance was found to increase linearly with \sqrt{t} . The absorbance was a linear function of silver in the glass, *i.e.*, Beer's law was obeyed, and diffusion coefficients could be calculated from Eq 2. The method is useful for colored ions only. It has so far been applied only to silver.

4. Electrical Conductivity

As the ionic composition of a glass changes during diffusion, its electrical conductance also changes since the mobilities of ions diffusing in and out are generally not equal. Measurements are commonly made by ac bridge methods using inert electrodes to avoid introduction of additional ions into the glass. The resistance of the molten salt is negligible compared to that of the glass. Various modifications of the experimental method have been reported (23, 49, 75, 82).

The relation between the change in electrical resistance and the diffusion coefficient of the ion diffusing in was first derived by Lengyel (49), although apparently incorrectly (23). Nevertheless, the linear relationship between resistance change and \sqrt{t} was confirmed by Doremus (23) who derived it in the form

$$\frac{R - R_1}{\sqrt{t}} = \frac{\sqrt{D_1}\sigma_1}{A} \int_0^{L/\sqrt{D_1t}} \left(\frac{\sigma_1 - \sigma}{\sigma} \right) dy \quad (\text{Eq 6})$$

where $y = x\sqrt{D_1t}$, R_1 and σ_1 are the original resistance and specific conductivity of the glass of area A and thickness L , and D_1 is the diffusion constant of the ion originally in the glass. The concentration profile has a constant shape as diffusion proceeds if $L \gg \sqrt{D_1t}$, a condition evidently satisfied in Lengyel's work.

5. Mechanical Deformation

When the ions exchanging across the glass-melt interface are not of the same effective size, *i.e.*, in all cases except self-diffusion, they may be expected to deform the silicate network and set up stresses in it. For example, it is well known that exposure of a sodium glass to lithium salts produces many small cracks due to the tensile stresses in the lattice which tends to shrink around the smaller ions. Correspondingly, the substitution of a larger for a smaller ion will produce compressive stresses.

The effect of these stresses can be seen in the bending of flat glass plates occurring during diffusion of ions into them. The relation between the amount of bending of the plate and the stress in it has been derived (42). Using Timoshenko's equation

$$M = \frac{Eb^3(1 + \nu)}{12(1 - \nu^2)r} \quad (\text{Eq 7})$$

where M is the bending moment uniformly applied around the edges of the plate, E = Young's modulus, b = thickness, ν = Poisson's ratio, and r = radius of curvature, Kistler derived the equation

$$w = \frac{E}{8p} \frac{1 + \nu}{1 - \nu^2} \frac{b^2}{r^2} = \frac{Kb^2}{r} \quad (\text{Eq 8})$$

where w is the amount of a larger ion diffusing into 1 mm^2 of the glass containing a smaller ion, and p is a constant depending on the relative volumes of the exchanging ions. Interference methods were used to measure the warping of thin, initially optically flat disks. Weight-gain experiments were correlated with the mechanical deformation.

The effect of stresses can also be seen directly in the polarization microscope (77). Tensions and compressions can be clearly distinguished.

B. CHARACTERISTICS OF IONIC DIFFUSION IN GLASS

Whether and how rapidly cations from molten salts will diffuse into glass appears to depend on the following factors: (1) size and charge of the ion in the melt, (2) ionic content of the glass, (3) the melt anion, and (4) temperature.

1. Dependence of Diffusion on the Nature of the Salt

Since most glasses which have been used for diffusion studies are of fairly complicated composition, it is difficult to compare the results of different authors. Except for cases in which the glass composition was varied systematically, most workers have employed silicate glasses whose major ionic constituent is sodium (5-20%) with minor constituents K, Ca, and Al. Clearly sodium is then the chief exchanging ion. Since the relevant experimental studies have been critically reviewed in detail (22), the results are summarized only briefly.

The exchange of silver from its molten salts for sodium in the glass was first studied by Schulze (75), who re-established this exchange as being 1:1 and confirmed the applicability of Fick's Law to the process. After Halberstadt (32) claimed that silver atoms could diffuse from silver sheet into glass, Kubaschewski (44) showed that under these conditions oxygen must be present for diffusion to occur. Below 30 torr O_2 the diffusion rate decreased rapidly to zero, proving that silver ion is the

diffusing species. Silver salts have been used by several authors (23, 38, 48, 68, 72) to study various aspects of the process because silver lends itself particularly well to analytical methods, and because the exchange of silver for sodium produces relatively larger weight changes than other ions.

Copper diffuses into glass from both CuSO_4 (38a) and Cu_2Cl_2 (68), but even the exchange from CuSO_4 is 1:1 with sodium, from which Cu(I) has been claimed to be the diffusing species; however, the validity of the former results (38a) has been questioned (22).

Lithium, sodium, and potassium diffuse into glass (22, 42, 49, 52, 77, 78, 89), the diffusion being most rapid when the smaller ion is in the melt and the larger one in the glass. For example, sodium easily diffuses into a potassium glass, but potassium penetrates into a sodium glass only slowly. Of the other monovalent ions, only thallium (68) and cesium (69) have been reported to diffuse into glass. Of the divalent ions strontium was reported to diffuse into a sodium glass (69); of the higher valent ions diffusion of vanadium from V_2O_5 was detected (68); but no diffusion from the following salts seemed to occur: CrCl_3 , PbCl_2 , AuCl_3 , PtCl_4 , Co_3O_4 , and FeCl_3 (68). In general, the diffusibility of ions into glass decreases with increasing size and charge. This effect is illustrated by the values shown in Table I for the diffusion coefficients of several

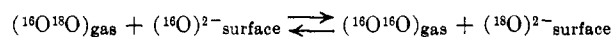
TABLE I
DIFFUSION COEFFICIENT

Ion	D , cm^2/sec	r +, A
Li^+	4×10^{-7}	0.6-0.78
Na^+	1.1×10^{-10}	0.95-0.98
Ag^+	2.5×10^{-10}	1.13-1.26
K^+	3×10^{-12}	1.33
Cs^+	4×10^{-13}	1.65-1.69
Sr^{2+}	3.1×10^{-13}	1.15-1.27

ions into sodium glasses of similar composition at 350° (6, 48, 69), *i.e.*, below the transformation region. The effect of size is probably related to the difficulty of accommodating a large ion in the silicate structure. The diffusion of multivalent ions is hindered by the requirement that the glass remain electrically neutral. Since the more mobile ions in the glass are usually monovalent, the exchange of two or more of these ions for each ion diffusing in would be required. The probability of such an occurrence is undoubtedly low. One mechanism by which multivalent cations from the salt phase could diffuse into glass without requiring an exchange with ions in the glass would be the simultaneous diffusion of anions, this being equivalent to the net diffusion of neutral "molecules" into the glass. No test for this mechanism involving multivalent cations seems to have been carried out as yet. It is generally assumed, however, that the negative oxide ions in the glass structure would repel anions from the melt. One experimental test (83) in which KBr was

equilibrated with Vycor glass at 800° gave no evidence for bromide ion diffusion into glass. More experiments with salts having more mobile cations and smaller anions, *e.g.*, NaF and LiF, would, however, be of interest. The well-known volatilization of NaF during the melting of feldspar-containing glasses suggests that fluoride ion may also be mobile in glass at lower temperatures.

One anion which is known to be mobile in glass, at least above 300° , is oxide. Indeed, the reversibility of the oxygen electrode to oxide ions in molten glasses (73) depends on this mobility. The use of O^{18} tracer (93) has also established that exchange between oxygen molecules in the gas phase and oxygen in fused silica occurs (900 - 1200°). On the basis of energetics, Sucov (93) has argued that this exchange involves singly bonded oxygen in the glass which "evaporates" interstitially to the surface where exchange takes place



The $(^{18}\text{O})^{2-}$ is now part of the surface and moves into the solid at a rate controlled by bulk diffusion. Hydroxyl ions also diffuse through glass and are involved in the diffusion of H_2O and H_2 . The extensive literature on the diffusion of these species has been reviewed recently (48a).

Rötger (74) has suggested that Na_2O "molecules" are mobile in glass, the mobility of the more strongly bound oxide ions controlling the rate. More convincing evidence for the net diffusion of metal oxides from silicates out of the glass comes from studies of the volatilization (21, 98, 106) of various oxides. The rates increase markedly with the metal content of the glass. Despite all this evidence for the mobility of oxides within glasses and the diffusion of electrically neutral oxides out of it, the question as to whether oxide ions can diffuse into the glass from molten salts and oxides apparently has not been answered experimentally. If the glass initially is pure fused silica there will be no cations in it which can exchange with those in the melt so that the latter can only enter the glass by migration into some kind of holes. Oxide ions can enter in two ways: by net diffusion, *i.e.*, by a change in the oxidation state of Si, and/or by an exchange reaction analogous to that for O_2 molecules. Tracer experiments could certainly be used to settle this question.

2. Effect of Glass Composition on Diffusion Rate

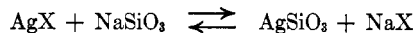
Since the predominant mechanism for ion diffusion into glass is exchange, the rate of this process must depend on the mobility of the ions initially in the glass as well as those in the melt. This will be true particularly when the ion in the melt is the more mobile. Systematic studies of this kind have been carried out by relatively few workers.

When the glass initially contains only sodium, the exchange rate with ions in the melt increases with the sodium ion concentration both for self-diffusion (41) and foreign ions (38a). Le Clerc (48) used radioactive tracers to study the diffusion of sodium, lithium, potassium, and silver into two glasses at 300°, one 13.4 mole % in sodium, the other 13.4 mole % in potassium. The diffusion of lithium into the sodium glass was much more rapid than into the potassium glass. More extensive and precise results were obtained by Sendt (78) who studied the self-diffusion of sodium and potassium, as well as lithium diffusion, into a series of glasses varying in the Na⁺/K⁺ ratio, but with (Na⁺ + K⁺) constant. The diffusion profiles and the diffusion constant were obtained at 626° by using tracers and an etching method. D_{Na^+} decreases by a factor of 20 as the glass composition changes from 13.8 mole % Na⁺ to 13.8 mole % K⁺, whereas D_{K^+} is virtually independent of glass composition. In the sodium-rich glasses lithium exchanges primarily with sodium, the K⁺ ion hardly participating. Only as the ratio K₂O/Na₂O reaches 3:1 does the exchange lithium-potassium become appreciable. Similar results were obtained for copper diffusion into a series of Na-K glasses (38a). The diffusion coefficient of Cu in the 520-600° range increased sharply with rising Na⁺/K⁺ ratio. D_{Cu} also depends on the divalent ions in the glass. The successive replacement of Ca in the glass by Sr and Ba reduces D_{Cu} to one-half and one-quarter of its value, respectively.

Interpretations of the effect of glass composition on diffusion rates are analogous to those for electrical conductivity in mixed glasses, except that in the latter there is no composition change. For example, Sendt (78) explains the decrease of D_{Na^+} with increasing K⁺/Na⁺ ratio in terms of K⁺ ions blocking the Na⁺-Na⁺ exchange. On the other hand, D_{K^+} remains independent of composition because the activation energy barrier for K⁺ is probably not particularly affected by introducing smaller ions into the glass. The exchanges Li⁺-Na⁺ and Li⁺-K⁺ in the mixed glasses appear to occur nearly independently, the total D_{Li} being the sum of the two processes. The two exchange rates depend on D_{Na} and D_K , respectively.

3. Effect of Melt Anion on Diffusion Rate

The question as to whether the melt anion affects the diffusion rate of the cation into the glass has received very little attention. For completely ionized salts it is difficult to visualize a mechanism for such an effect. However, Richter (72) observed quite large differences in the depth of penetration of silver ions into several silicate glasses from halides, the sequence being Cl > Br > I. The distance travelled by the silver ions from AgCl was six times as great as from AgI. Richter attributes the difference to an equilibrium



which lies further to the left, the larger the anion; but this explanation would require that the concentration of free silver ions in AgI is very much less than in AgCl, and that the displacement of the equilibrium $AgX \rightleftharpoons Ag^+ + X^-$ to the right is the factor limiting the availability of Ag⁺ for diffusion. Neither of these conditions is likely. Further work is thus needed to verify the existence of the phenomenon.

4. Effect of Temperature on Diffusion Rate

Since diffusion is a rate process, its temperature dependence is expected to follow the Arrhenius relation

$$D = D_0 e^{-E_a/RT} \quad (\text{Eq 9})$$

i.e., log D is linear in $1/T$ if the activation energy E_a is independent of temperature. This latter condition usually does not hold in the glass transition region, however. Thus Richter (72) found two distinct slopes for silver diffusion into flint glass, the temperature of slope change being that of the known transformation.

Johnson, Bristow, and Blau (7, 41) noted changes in slope near 485°, *i.e.*, in the transformation region. Both above and below this region the slopes of log D vs. $1/T$ are smaller than in this region. The authors discuss these changes in terms of the absolute reaction rate theory (see section IVD). On the other hand, Ito (38) found only a single activation energy of 110 kjoules (26.3 kcal) for the diffusion of silver into a sodium glass, but all his measurements seem to have been below the transformation region.

Ralkova (69) observed S-shaped log D vs. $1/T$ plots for the diffusion of both Cs⁺ and Sr²⁺ into a Na⁺-K⁺ glass. Various portions of the curve are only approximately linear. The steep portion of the curve falls in the transition region. Thus for Cs⁺ and Sr²⁺ diffusion, the following activation energies were obtained.

	E_a , kjoules/mole (kcal/mole)		
	300-350°	350-400°	500-600°
Cs ⁺	32 (7.6)	127 (30.7)	23 (5.6)
Sr ²⁺	63 (15.0)	205 (49.0)	29 (7.0)

As might be expected, values for Sr²⁺ are greater than for Cs⁺ in all three regions. Earlier results (48) on the anomalous temperature dependence of Li⁺ diffusion have recently been confirmed and extended (66a). Up to 50° below the transformation temperature T_g , D_{Li^+} rises unusually rapidly, then goes through a sharp maximum and drops to a minimum at T_g . Above T_g the diffusion increases normally. The low-temperature results are accounted for in terms of cracks which form in the glass as a result of the stresses caused by the Li⁺-Na⁺ exchange; *i.e.*, the effective surface area is increased. With rising temperature the viscosity decreases and the cracks close since the glass can respond to stresses by flowing. Above T_g the

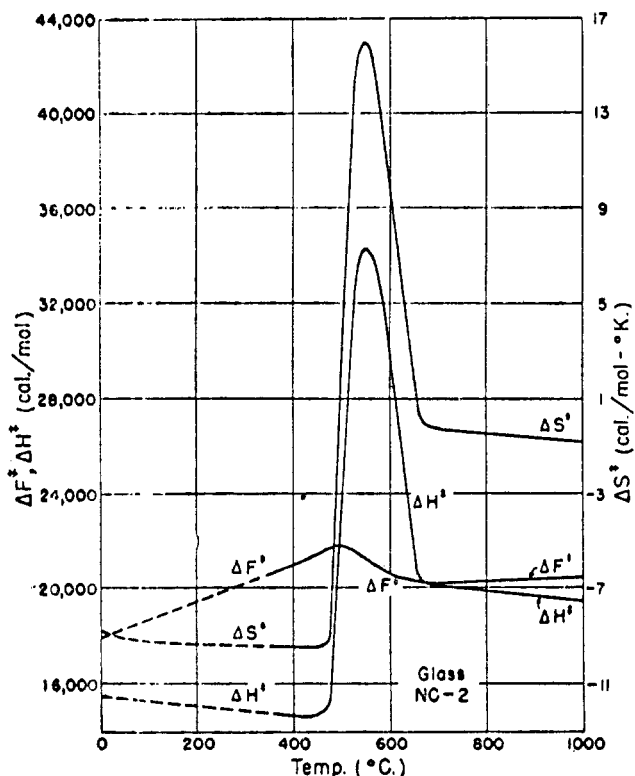


Figure 1. Diagram showing activation parameters for diffusion ΔF^* , ΔH^* , ΔS^* vs. temperature of a sodium silicate (21% Na_2O) glass ($\lambda^2 = 7 \times 10^{-16} \text{ cm}^2$ assumed constant, from ref 41) (reproduced by permission of the copyright owners).

surface area is constant and the diffusion rises in accordance with Eq 9.

C. THEORIES OF THE DIFFUSION MECHANISM

The observation of a linear dependence of $\log D$ on $1/T$ for at least limited temperature regions suggests the treatment of the process in terms of the activated state concept implied in the Arrhenius equation (Eq 9) and elaborated in the absolute reaction rate theory of Eyring which has been successfully applied to diffusion in molecular liquids and molten salts (8). Ionic diffusion in glasses has been analyzed in terms of this theory (41). The diffusion constant in terms of the absolute reaction rate theory is

$$D = \lambda^2 \frac{kT}{h} e^{-\Delta F^*/RT} = \lambda^2 \frac{kT}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R} \quad (\text{Eq 10})$$

where λ represents the average distance between two equilibrium positions of the diffusing ions. The Arrhenius activation energy is

$$E_a = RT + \Delta H^* - p\Delta v^* \quad (\text{Eq 11})$$

where Δv^* is the increase in volume accompanying activation. This term is negligibly small for glasses, but not for molten salts. From the temperature dependence of D , the product $\lambda^2 e^{\Delta S^*/R}$ can be calculated, but in order to calculate ΔS^* the jump distance λ must

be known. In the diffusion of sodium into a soda lime-silica glass, $\lambda^2 e^{\Delta S^*/R}$ was found to go through a large maximum at 550° which could only be accounted for by a corresponding maximum in ΔS^* since λ is expected to be fairly temperature independent. From model considerations a distance of 2.65 Å was chosen and ΔS^* , ΔH^* , and ΔF^* could then be calculated as a function of temperature. A plot of these three quantities (Figure 1) shows a pronounced maximum in the transition region, being nearly constant over a several hundred degree range both below and above this range. Ions in glass move primarily by a vacancy mechanism. The details of this vacancy mechanism have recently been discussed in considerable detail (14, 22). Defects are formed by moving a cation from one oxygen to another, giving one oxygen with no cations and another one associated with two. Diffusion then occurs by the movement of a cation from an oxygen with two cations to an oxygen with one. The activation energy for this process is lower than for the movement of the vacancy which would require removing a cation from an oxygen having only one cation. Calculated jump distances λ are in the range 0.9–3.2 Å, reasonable for this model and in agreement with the 2.65-Å value quoted by Johnson, Bristow, and Blau (41).

Since the nature and size of monatomic cations is essentially independent of temperature in the range of interest, the explanation for the temperature dependence of the activation energies must be based on changes in the glass network. Below the transition the glass is essentially a rigid structure, motion of the network being confined to thermal vibrations about their equilibrium positions. The "holes" in the network are thus relatively fixed in size and shape and randomly distributed in the glass framework. As the ion moves from one hole to another it is momentarily in a more ordered position, leading to a decrease in entropy, $\Delta S^* < 0$. As the temperature rises into the transformation range the network structural units relax into positions of lower energy if sufficient time is allowed at any one temperature for the relaxation to occur. The experimental diffusion time becomes comparable to that required for the network tetrahedra to flex at their shared corners. The ions now influence the size and shapes of the holes in which they lie in such a way that the structure is more ordered when the ions are in their equilibrium positions. Consequently, ΔS^* becomes more positive. Above the maximum the glass approaches more and more to the liquid state in which momentary breaking of bonds with partial rotation of the network tetrahedra can occur. The equilibrium and activated states of the diffusing ions thus become more similar and both ΔH^* and ΔS^* decrease.

Some preliminary evidence was also obtained (41) which indicates that ΔS^* is an increasing linear function of sodium concentration in the glass, indicating

a tendency toward greater sodium-equilibrium configurational order. Simultaneously ΔF^* decreases, connoting lower barriers to sodium migration.

The above discussion assumes that the number of mobile ions is independent of temperature. If this were not so, Eq 10 would have to be modified by introducing a concentration term which might alter the curves in Figure 1.

D. DIFFUSION AND CONDUCTANCE. THE NERNST-EINSTEIN EQUATION

In recent years the question of the validity of the Nernst-Einstein equation has been discussed for both molten salts and glasses. The rationale underlying the equation is that the mechanisms of ionic mobility for both diffusion and mobility are similar; thus the ionic mobility for self-diffusion

$$u_i = \frac{D_i}{RT} \quad (\text{Eq 12})$$

and for conductance

$$u_e = \frac{\sigma_i}{Z_i^2 F^2 C_i} \quad (\text{Eq 13})$$

where σ is the specific conductance, Z_i the charge, F the Faraday, and C_i the concentration. If the Nernst-Einstein equation is valid $u_i = u_e$ and

$$\sigma_i = \frac{Z_i^2 F^2 D_i C_i}{RT} \quad (\text{Eq 14})$$

or, since $\sigma_i = \lambda_i C_i$

$$\frac{D_i}{RT} = \frac{\lambda_i}{Z_i F^2} \quad (\text{Eq 15})$$

Since eq 15 implicitly contains transport numbers ($\lambda_i = t_i \Lambda$), the partial conductances can be combined (94a) to give

$$\frac{Z_1 D_1 + Z_2 D_2}{RT} = \frac{\Lambda}{F^2} \quad (\text{Eq 16})$$

The validity of the equation can, of course, be tested experimentally, but the explanations for the deviations depend on the model used for ionic mobilities.

1. Molten Salts

The Nernst-Einstein equation holds for electrolytic solutions at infinite dilution (but not for finite concentrations) and is almost exactly obeyed for ionic crystals. However, the conductances predicted from self-diffusion data are considerable higher than the experimental values (11) for molten salts.

Although there has been considerable discussion over the theoretical treatment of this difference, there is general agreement that there must exist modes of motion in diffusion which do not contribute to con-

ductance. The "quasi-random model" (46) is based on the application of the Onsager reciprocal relations. It results in the calculation of friction coefficients for the interactions $++$, $--$, \pm , the last accounting for drag effects of ion pairs. This model has been criticized for yielding results in disagreement with experiment (8). Diffusion has been interpreted in terms of a quasi-lattice model in which the volume increase on melting is explained in terms of an increasing number of holes or vacancies with rising temperature (8, 10, 11). In terms of this model the Nernst-Einstein equation applies to the single ionic species in the molten salt, but the motion of coupled anion-cation (ion-pair) vacancies contributes to diffusion but not conductance. For example, in NaCl approximately 10% of the cation and anion sites are vacant, the rest of the structure having slightly irregular NaCl packing. Half the total transport of Cl and one-fifth that of sodium are accounted for by the coupled vacancy mechanism.

2. Glasses

The question as to whether the Nernst-Einstein equation holds for glasses has been treated both experimentally and theoretically. Very few studies of either kind have been reported, however.

The measured electrical conductivity (27) of a simple sodium silicate glass was less than that calculated from the diffusion data (41) by a factor of 2-3, a situation similar to that for molten salts. These results could be interpreted either in terms of the transport number $t_{\text{Na}^+} < 1$, or by a mechanism which accounts for the difference in terms of the two kinds of processes. The first possibility can probably be ruled out for a simple sodium glass in which there are no other mobile cations. The mechanism has usually been discussed in terms of a correlation factor f used to modify the Nernst-Einstein equation

$$D = f \frac{RT\sigma}{Z^2 F^2 C} \quad (\text{Eq 17})$$

where f depends on the structure of the substance and on the transport mechanism. For diffusion in crystalline solids $f = 1$ if diffusional motion is completely random, but less than unity if the jumps or steps of the diffusing particles are correlated, as in a vacancy mechanism (2, 15). This kind of correlation, that the probability of a jump in a certain direction depends on the direction of the previous jump, does not exist for electric conduction.

The above ideas have been applied in considerable detail (34) to ionic diffusion in glasses. Several types of transport mechanisms are distinguished by which ions can move through the glass network.

The values of f are very sensitive to rather small changes in glass composition. It follows that the de-

termination of f from diffusion and conductance measurements on the same system is a sensitive tool for the study of transport mechanisms both in molten salts and glasses, but nothing appears to have been done yet in applying the above ideas to the glass-molten salt interface.

Since diffusion coefficients of even mobile ions are several orders of magnitude less in the glass (10^{-9} – 10^{-11} vs. 10^{-5} cm²/sec in salts), the more viscous medium must control the diffusion rate of ions across the interface. Nevertheless, the region of the glass near the surface might differ somewhat from the interior, owing to the presence of the salt. Diffusion profiles and potential studies on glass electrodes (*cf.* section VIII) strongly suggest this.

E. APPLICATIONS

Although diffusion of ions into glasses has been studied for more than 50 years, the total literature in this field is not large. It is not surprising, therefore, that at this stage of development only a few applications have been suggested.

In recent years the ion exchange occurring at glass-vapor boundaries has been used for chemical surface modification, *e.g.*, hardening. For example, if a sodium glass is heated in SO₂-H₂O vapor it loses sodium which is replaced by protons (77).

Recently surface hardening has been accomplished by immersing glass into a salt bath consisting of 95 wt % Li₂SO₄ and 5% Na₂SO₄ (90). Treatment for several minutes at temperatures in the 860–900° range of a SiO₂-Al₂O₃-TiO₂ glass increased the strength markedly. The lithium ions in the melt then exchange for the sodium ion in the glass. If this exchange occurs above the strain point the resultant shrinkage of the structure will not crack the glass. The final result is a crystalline surface layer consisting of a solid solution of β -eucrypte (Li₂O·Al₂O₃·2SiO₂) and quartz which has a very low expansion coefficient. One of the best methods for strengthening glass is to compress its surface layer by exchanging smaller ions (Li⁺, Na⁺) in it for larger ions, *e.g.*, K⁺ in the molten salt bath (12a, 42).

Diffusion of radioactive materials into glasses has been suggested as a possible method of waste disposal (69). It is necessarily limited to mobile ions. The disadvantage of low diffusion rates might be overcome by carrying out the process at high temperatures and then cooling the glass to prevent the ions from diffusing out.

Since glass membranes are ion selective they might be used for quantitative separations by using an applied field. Thus the more mobile cations in the mixture would be transported through the membrane and the slower ones left behind.

Perhaps the largest contribution which the study of

diffusion processes across glass-molten salt interfaces has made is to the understanding of the operation of electrochemical devices using glass membranes. These are discussed in section VII.

V. ELECTRICAL CONDUCTANCE

Cavendish (13) appears to have been the first to discover that, although glass is an insulator when cold, it increasingly conducts electricity as the temperature is raised. His experimental arrangement, destined to be repeated with various modifications by many investigators, consisted of placing a mercury-filled glass tube into a trough filled with mercury and applying a voltage between the two glass-separated mercury pools. The experiment seems to have been ahead of its time for it was not repeated until 1854 (3, 12). The early work is summarized by Warburg (101) who began systematic researches in this field.

Most of the early experimenters and many of the more recent ones employed high dc voltages and measured the resulting resistance and/or current changes; *i.e.*, the measurement itself irreversibly altered the material being studied. These changes appear to be of two kinds: (a) a decrease in the concentration of mobile ions which are transported out of the glass under the influence of the field; and (b) changes in the chemical nature of the silicate network, such as oxidation of oxide ions to oxygen, reduction of Si⁴⁺ to Si³⁺, introduction of OH⁻ from the surrounding atmospheric water, etc.

In order to avoid such composition changes ac measurements are clearly required and have been increasingly employed. In addition to Ohm's law type information, they also yield some details of glass structure through the frequency dependence. In addition, the temperature coefficient of conductance can also be interpreted in terms of activation energies for ionic migration.

A. THE CONDUCTION PROCESS

Although ac measurement are preferable when composition changes are to be avoided, most of our knowledge of the conduction process comes, partly for historical reasons, from dc measurements. Since the ionic conductivity of glasses is generally low compared to molten salts and electrolytic solutions, application of a dc voltage for a short time does not lead to large composition changes.

Morey (63) has summarized much of this work which has led to the commonly accepted model for conduction in most glasses. Since this has been described previously by many authors (56, 58, 88), it is summarized only briefly. Up to fairly high temperatures the glass (*e.g.*, silicate) network is fairly rigid and resembles a polymeric disordered solid. Various size and shape channels occupy some of this network. Many

of these are dead-end, but the mobile small cations (Na^+ , Li^+) which occupy positions in low potential energy sites can find their way through this network over macroscopic distances. It is this phenomenon which accounts for the electrical conductance. As the size and charge of the constituent ions increases the conductance decreases. For ions containing only a single mobile cation the conductance increases with its concentration, but more rapidly than the concentration. This phenomenon has been interpreted as a loosening of the network (86). Mixed glasses generally exhibit a conductance minimum. This is discussed below in section VB.

The conductance of all glasses increases with temperature. Ever since the logarithmic nature of the increase was derived from the van't Hoff equation (70)

$$\kappa = A \exp(-E_{\kappa}/RT) \quad (\text{Eq 18})$$

values of the activation energy E_{κ} have been used in the interpretation of transport mechanisms. Most glasses exhibit inflections in the $\ln \kappa$ vs. $1/T$ curve in the transformation region which correspond to changes in E_{κ} and hence corresponding changes in mechanism. For some glasses Eq 18 holds over the entire temperature range. For others, particularly in the molten state, the resistivity is represented by

$$\ln \rho = A + BT + CT^2 \quad (\text{Eq 19})$$

Equation 18 suggests an interpretation in terms of an activated state in which the mobile ion randomly jumps over a characteristic distance λ from one equilibrium position to the next, the motion occurring preferentially in the direction of the field. The consequences of such a model have been worked out (86). If the width of the potential barrier is assumed to be temperature dependent (the structure expands when heated), both Eq 18 and Eq 19 follow as the low- and high-temperature limits, respectively (92).

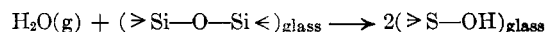
The question as to which ions can conduct current in glass does not seem to have been tested exhaustively. In glasses containing Na^+ and Li^+ these ions will conduct most of the current. As the charge and size of the ions increase, their mobility decreases greatly. For the moment it seems fair to assume that any ion which can diffuse can also migrate in an electric field. A list of ions known to diffuse and a more detailed discussion of transport mechanisms is given in section IVB1.

Although pure fused silica, *i.e.*, SiO_2 , contains by definition no mobile cations, all commercial silica conducts electricity, although its resistivity at room temperature is near 10^{19} ohms cm^{-1} (67). As the temperature increases this conductance rises according to Eq 18, but with several different activation energies over different temperature ranges. The conductance

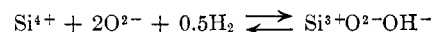
has recently been measured up to 2480° by Veltri (99) who also reviews older work.

Up to 1600° the activation energy is 96 kjoules (23 kcal), a value common to that for small cation conductance and therefore indicative of impurities. In the next range, E_{κ} rises to ~ 293 kjoules (~ 70 kcal), but no definite process could be associated with this value. In the highest temperature range E_{κ} is 364 kjoules (87 kcal), in agreement with the Si-O bond energy.

Most glasses, including fused silica, exhibit infrared spectra characteristic of OH groups. The intensity of the bands increases with time of exposure and with increasing H_2O vapor content of the atmosphere surrounding the hot glass (64). The diffusion of water occurs not molecularly, but by a dissociative mechanism (48a) in which the mobile species are OH groups, as shown below.



Similarly, in the presence of hydrogen gas an equilibrium of the type



is set up (4) so that the continuing diffusion of hydrogen produces the diffusion of hydroxyl also. This "water" content of the glass affects its electrical properties (64). For example, the conductivity of lead silicate glasses increases with water content (60). According to the authors the conducting species in these glasses is the Pb^{2+} ion, and the authors hypothesize that hydrogen bonding in the glass reduces the electronegativity of the oxide. Consequently the $\text{Pb}^{2+}\text{-O}^{2-}$ interaction is weakened and the activation energy for its conduction lowered. This mechanism might be expected to operate for cation-conducting glasses generally, but this has not yet been tested.

B. MIXED GLASSES

When the glass contains more than one mobile cation the total conductivity cannot be calculated by linear interpolation between the conductivities of the components (50, 51, 53). This phenomenon has been studied extensively for a series of binary silicate and borate glasses containing a constant total cation concentration of pairs of ions chosen from Li^+ , Na^+ , and K^+ or the divalent ions Ca^{2+} , Ba^{2+} , and Mg^{2+} (50c). In all cases the conductance exhibits a pronounced minimum although this is not usually symmetrical with respect to the concentration coordinate. A typical example is shown in Figure 2. Lengyel and Boksay have developed a theory based on a model that vacancies are statistically distributed in the glass, but their number is small compared to the total number of ions. The authors then calculate the probability that an ion of given size may enter a vacated site. This prob-

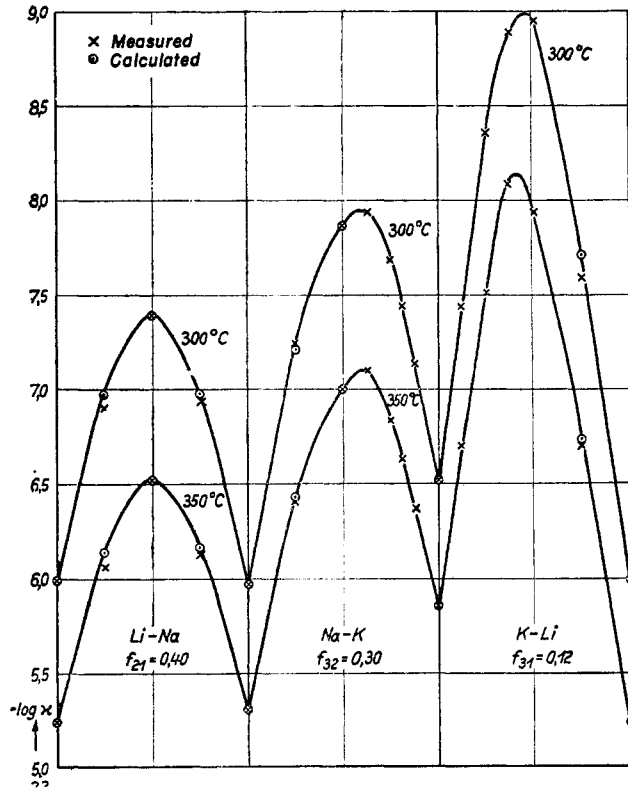


Figure 2. Specific conductance vs. composition isotherms for Li-Na, Na-K, and K-Li silicate glasses. Total alkali concentration in each glass is 16 mole %. Conductance calculated from Eq 20 (from ref 50c) (reproduced by permission of the copyright owners).

ability factor is $f = 1$ if a smaller ion enters the site vacated by a larger one, and $f < 1$ for the reverse situation. From this model the equation for the total conductivity is

$$\kappa = A^r(n_1F_1\kappa_1 + n_2F_2\kappa_2) \quad (\text{Eq 20})$$

where n_1 and n_2 are the mole fractions of ions 1 and 2 and κ_1 and κ_2 are the conductivities of the corresponding monocationic glasses. $r + 2$ is the number of steps needed to reach a stationary state, and A , F_1 , F_2 are complicated probability functions. Conductances calculated from the theory agree well with experiment.

Additional insight into the conductance mechanism can be gained from a study of transport numbers in these mixed glasses (51). As shown in Figure 3, the ionic transport number of the ion present in larger amount is always greater than its mole fraction. Particularly at the lower temperature the inflections in the curve are quite noticeable. When the smaller ion is present in excess the larger ions are isolated and can move only relatively infrequently since they are surrounded by small ions. In the reverse case the isolated small ions can easily occupy the site vacated by a large ion. However, since mostly large ions are available to occupy the site vacated by a small ion, the latter is more likely to reoccupy its original site.

Consequently its transport number will be smaller than its mole fraction. The effect of immobile divalent cations on the mobility of mobile univalent ions has also been studied (50e, 59). The larger the divalent ion the greater is the conductance decrease produced. The effect has been explained both as a filling up of voids by the divalent ion (50e) and in terms of the polarizing effect of the cation on the network oxygens (59), but both of these explanations seem to be *ad hoc* hypotheses.

When a cation-containing glass is placed in a molten salt so that cation exchange takes place, a mixed glass region is produced, at least near the interface. For example, when LiCl was added to NaCl equilibrated with Vycor glass (82), the conductance reached a steady value with each new addition. The steady-state conductance was a linear function of LiCl concentration. If the predominant mechanism is $\text{Li}^+ - \text{Na}^+$ exchange the increased conductance represents the difference in Li^+ and Na^+ mobility. The fact that no conductance minimum was observed in this glass of mixed composition implies that in this case the vacancy concentration is very high and the two ions are not hindered in their motion by a lack of vacant sites. The conductance minimum evidently occurs only when the ionic concentration is much larger than the number of vacancies. Conductance studies of glasses of varying ion content immersed in molten salts might thus be useful for studying the exchange mechanism.

VI. ELECTROLYSIS OF GLASS

When an electrical potential difference is applied across a glass containing mobile cations, these will migrate to the cathode. This process can be carried out in two ways: (a) if the migrating ions are replaced, *e.g.*, if the potential is applied to a sodium glass immersed in a molten sodium salt, no net composition change will occur in the glass; (b) if the potential is applied in such a way that the migrating ions are not replaced, *e.g.*, with glass between inert electrodes such as graphite, the net composition of the glass is changed as a result of the current passed and the process can be described as electrolysis. If electrolysis is defined as a process in which the composition of the glass changes as a result of an applied potential, then we must also include the replacement of the original ions in the glass by foreign ions in the melt. Much of the early work concerned with the nature of the conductance process (*cf.* 63) was carried out under electrolysis conditions.

These studies established the ionic nature of the conduction process in glass and provided much information as to the relative mobility of different ions. This topic was discussed in section V.

It was noticed that when a sodium glass is electrolyzed without replacement of the ions lost at the

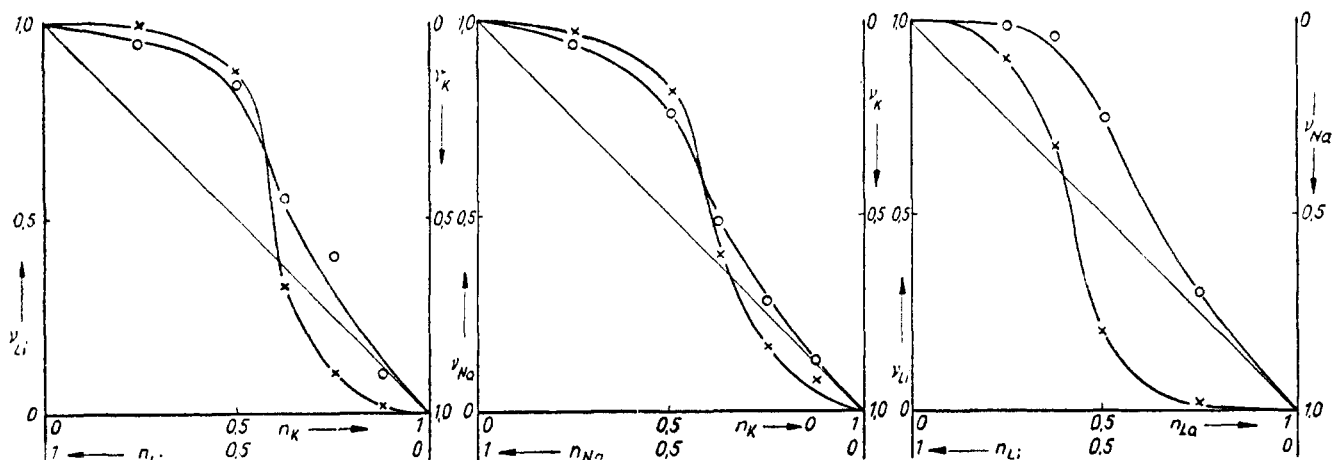
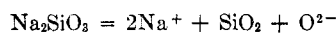


Figure 3. Transport numbers ν vs. mole fraction n_i of total ion content for the glasses of Figure 2: \times , 270°; \circ , 420° (reproduced by permission of the copyright owners).

cathode the resistance of the glass increases rapidly and this increase arises from the formation of a poorly conducting layer near the anode. Simultaneously with the reduction of sodium at the cathode, oxygen gas appears in and may be evolved from the anode layer of the glass (47, 65, 76). From this point of view the glass is regarded in terms of the equilibrium



and the electrolysis produces the migration of sodium to the cathode and oxide ions to the anode. The observation that O_2 gas may be trapped in the glass suggests that the electron transfer to the inert anode conductor (metal or graphite) may occur over considerable distances.

Gas evolution from the cathode was also observed but seemed to depend on the previous exposure of the glass to water vapor (65).

In recent electrolysis experiments of fused silica, a simultaneous study of the spectra has greatly aided detailed interpretation (35). The migration of mobile cations to the cathode appears to be accompanied by the introduction of protons at the anode. If the water vapor pressure is decreased the rate of electrolysis, *i.e.*, the movement of the anode layer boundary, likewise decreases. These protons give rise to hydroxyl groups as Si-OH in the glass which cannot even be removed by heating under vacuum. The detailed behavior of fused silica during electrolysis also depends on imperfections in the glass structure. For example, if silicon is coordinated by three oxygens its formal valence is $3+$ and it may be oxidized to $4+$ by electrolysis. In addition, immobile impurities such as Al^{3+} also affect the rate of hydroxyl diffusion.

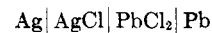
When the electrode consists of metals whose ions can diffuse into glass, *e.g.*, Au, Ag, Cu, Pd, they do, replacing the original alkali metal impurities (24). The effect is similar to that for cation migration from molten

salts except that ions must first be produced, presumably by reaction with oxygen. If the fused silica is made from acicular quartz crystals the migration is anisotropic, being most rapid in the direction of the original quartz crystal *c* axis.

VII. ELECTROCHEMICAL POTENTIALS AT GLASS-MOLTEN SALT INTERFACES

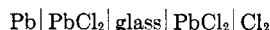
When a glass-molten salt interface is formed a potential difference will exist across it. This potential arises from the selectivity of the glass for certain ions in the melt and from differences in the mobilities of various ions in the glass. The theory of these interfacial (membrane) potentials is thus related to the diffusion and ion-exchange processes discussed in section IV.

Tamman (95) was apparently the first to construct a galvanic cell in which two molten salts were separated by a glass membrane. He was primarily interested in the study of Daniell cells and wished to prevent bulk mixing. However, he observed that the difference between the cells



with and without membrane was approximately 250 mv. In a more detailed investigation of this phenomenon (31) it was observed that when the same salt was present on both sides of the glass the potential was the same as in the absence of the glass. Thus, the emf of the formation cells $\text{Ag}|\text{AgCl}|\text{Cl}_2$ and $\text{Ag}|\text{AgCl}|\text{glass}|\text{AgCl}|\text{Cl}_2$ was nearly the same. It is this fact which makes glass membranes useful in the measurement of formation cells in which direct reaction between anode and cathode must be prevented. When the salts on the two sides of the glass are not the same, an additional potential difference arises which Grube and Rau attribute to the difference in transport mechanism between the salt-salt interface (anionic) and the salt-

glass interface (cationic). Nevertheless, results of glass membrane cells could be used to calculate the potential of a Daniell cell without glass. For example, the difference in emf of the cells



and

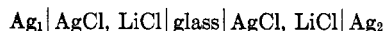


is equal to the emf of the Daniell cell $\text{Pb}|\text{PbCl}_2|\text{AgCl}|\text{Ag}$.

The first measurements on fused salt concentration cells with glass membranes were reported by Elkins and Forbes (26) who used AgCl-alkali chloride mixtures and Pyrex glass. They defined an ionic "transference constant" K by assuming that if two cations, *e.g.*, Ag^+ and Li^+ , carry current across the salt-glass boundary the ratio of currents is given by

$$I_{\text{Ag}^+}/I_{\text{Li}^+} = K_{\text{Ag}^+}N_{\text{AgCl}}/K_{\text{Li}^+}N_{\text{LiCl}}$$

The emf of the concentration cell



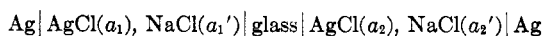
then is

$$E = (RT/F) [\ln (a_1/a_2)_{\text{AgCl}} + \ln (\sum K'a)_2 / (\sum K'a)_1] \quad (\text{Eq 21})$$

where K' is substituted for K when activities are used instead of mole fractions and the summation extends over both AgCl and LiCl. The transference constants are similar to but not identical with the usual ionic transport number since the $\sum K \neq 1$. K values were somewhat concentration dependent, but this was very much less than the difference between different ions.

More recently concentration cells with glass membranes using AgCl-alkali chloride electrodes have been reinvestigated, particularly with applications to reference electrodes in mind (54, 81, 84, 85).

When the alkali metal cation is sodium, a simple modification of the equation for a concentration cell with liquid junction is adequate to account for the results. Thus, for the cell



$$E = (RT/F) [\ln (a_2/a_1) - \int_{a_1}^{a_2} \sum_i t_i d \ln a_i] \quad (\text{Eq 22})$$

where the a 's represent activities on the mole fraction scale and the t_i 's are cation transport numbers for which $\sum t_i = 1$. If t_i depends only on the selectivity of the glass for cations and is independent of melt composition

$$E = (RT/F) [\ln (a_2/a_1) - t_{\text{Ag}^+} \ln (a_2/a_1) - t_{\text{Na}^+} \ln (a_2'/a_1')] = (RT/F) t_{\text{Na}^+} \ln [(a_2/a_1)(a_1'/a_2')] \quad (\text{Eq 23})$$

A test for the assumptions made in the derivation lies in the linearity of a plot of E vs. the logarithmic term.

This linearity holds when more than 2 mole % sodium is present in the system, indicating that this ion is then the chief charge carrier, but not when KCl and CsCl are substituted (85). In that case sodium ion impurities carry varying and indeterminate fractions of the charge.

Relatively little is as yet known of the mechanism by which a membrane potential is established, *i.e.*, the details of the ion-exchange processes occurring across the interface and the structure of the interface region. However, the potential drop across a glass immersed in a molten salt which arises from the difference in the diffusion coefficients of the exchanging ions has been derived (23).

The total potential drop V across the interface is given by

$$V = \int_0^L E dx = \frac{RT}{F} \ln \left\{ \frac{1 + N_L[(D_1/D_2) - 1]}{1 + N_0[(D_1/D_2) - 1]} \right\} \quad (\text{Eq 24})$$

where E is the potential gradient, N_L and N_0 are the mole fractions of ion 1 at the respective surfaces, and the constancy of D_1/D_2 with changing N_1 has been assumed in the integration. V is independent of the shape of the diffusion profile, the time of diffusion, and the absolute values of concentrations and diffusion coefficients. Thus the potential becomes constant as soon as ionic equilibrium is reached on the surface.

Equation 24 can be used to examine data on the cell $\text{Ag}|\text{AgCl}(0.038), \text{NaCl}(0.962)|\text{Vycor}|\text{AgCl}(x), \text{NaCl}(1-x)|\text{Ag}$ which was measured for $0.132x \leq 1.00$ (81). In terms of Eq 23 t_{Na^+} in this cell is a constant over nearly the entire range of concentration. Its value is approximately unity, indicating that Na^+ carries most of the charge through the glass. However, D_1/D_2 calculated from Eq 24 varies with composition as shown below.

N_0	V , mv	D_1/D_2
0.015	0.373	59.2
0.060	0.222	12.1
0.160	0.130	4.8
0.295	0.071	2.7
0.515	0.043	2.3
0.868	0.010	2.2

If the assumptions made in the derivation of Eq 24 are valid, the above calculation indicates that D_1/D_2 is constant only when the melt on both sides of the glass is rich in NaCl. As the melt on one side of the glass becomes low in NaCl, its diffusion constant becomes greater relative to silver. This conclusion appears to be inconsistent with one of the assumptions made on the derivation that D_1/D_2 is independent of N_1 . This dependence may account for the differences in the D_1/D_2 values found by Doremus (23) and Schulze (75). One interesting technique consists of studying concentration cells whose entire emf is a membrane potential.

For example, if in the AgCl-NaCl cell discussed above $X_1 = X_2 \simeq 1$, *i.e.*, nearly pure AgCl on both sides, the entire emf will arise from the second term of Eq 22, even when the actual concentrations are very small. This method was first used by Lengyel and Sammt (52) who added quantities of NaCl, KCl, and LiCl to PbCl₂ in concentrations as small as 10^{-5} mole fraction. With NaCl in the melt and a sodium glass, the emf was accounted for by setting $t_{Na^+} = 1$, *i.e.*

$$E = (RT/F) \ln X_{NaCl(2)}/X_{NaCl(1)} \quad (\text{Eq 25})$$

but similar experiments with KCl and a potassium glass gave potentials which were time dependent, the slope of the steady-state values varying with experiment and being less than RT/F . The response of a mixed Na-Li glass to lithium ions in the melt was nonlinear.

Recently this work has been repeated using AgCl as the major constituent and fused silica glass whose alkali metal ion impurity is <15 ppm (83). In this case the exchange of ions in the glass for those in the melt must be extremely small. Nevertheless, the results qualitatively resemble those of Lengyel and Sammt (52). Both the size of the alkali metal ion and the presence of ions previously added determine the emf. In general, the smaller ions are more effective than the larger ones in establishing a potential response. For example, the emf responds to the addition of KCl only if no NaCl and LiCl have been added previously, and even then only with a slope corresponding to $t_{K^+} = 0.3$. The subsequent response to K⁺ is completely obliterated by addition of NaCl or LiCl. The fact that stable potentials are more slowly established the larger the cation and the greater the concentration of ions previously added shows clearly that the composition of the glass layer adjacent to the melt is crucial to the establishment of a membrane potential.

Laity (45) has pointed out that when melts containing sodium ions are present on both sides of a sodium glass there will be an interfacial potential at each boundary of the form

$$E = -(RT/F) \ln \frac{a_{Na^+(melt)}}{a_{Na^+(glass)}} \quad (\text{Eq 26})$$

The total membrane potential is then the sum of two such terms with signs reversed

$$E = (RT/F) \ln \frac{a_{Na^+(melt 2)}}{a_{Na^+(melt 1)}} \quad (\text{Eq 27})$$

which is independent of glass composition. This independence will hold only if the glass composition of the two interfacial regions is the same, particularly with respect to the charge-carrying ions.

The importance of the glass composition near the interface is also shown by the existence of asymmetry potentials which frequently occur even when the same salt is present on both sides of the glass. They are

generally attributed to an unequal distribution of sodium ions arising during glass blowing owing to the volatility of Na₂O (*cf.* section IVE) and decrease with time. When LiNO₃ was present on both sides the emf built up initially to several tenths of a volt but decreased to nearly zero (71).

VIII. GLASS MEMBRANE REFERENCE ELECTRODES

Reference electrodes are as important for electrochemical measurements in molten salts as in aqueous solutions, but the high temperatures cause greater difficulties in the design of electrodes which are mechanically sturdy and remain stable and reproducible for long periods of time. Moreover, since there exists no commonly accepted zero reference analogous to the standard hydrogen electrode in aqueous solution, it is not surprising that this field is not yet as far advanced. Stability and reproducibility have been emphasized, rather than establishment of electrode potentials on a thermodynamic scale.

Since liquid junctions between the reference melt and the solution under study are difficult to maintain, glass membrane electrodes have found increasing use (1). All glass membrane electrodes depend for their operation on the ionic conduction of glass, usually by sodium. Other mobile ions, such as lithium, which may diffuse into the glass during its immersion into the salt melt, may also conduct current.

Glass electrodes may be conveniently classified according to (a) the electrode reaction or events occurring inside the glass electrode, and (b) the ion which carries current through the glass; *i.e.*, the ions involved in a and b may be the same or different. Most electrodes which have been described in the literature so far fall into one of three categories.

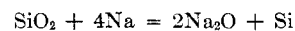
	Electrode reaction	Transport in glass
1	sodium	sodium
2	ion of low mobility in glass	sodium or other mobile ion
3	indeterminate	mobile ion

A. SODIUM-GLASS ELECTRODES

All sodium glass electrodes are of the type

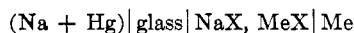
Na or Na alloy	glass containing Na ⁺	melt containing Na ⁺
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The reactivity of sodium creates considerable problems, particularly at high temperatures. Sodium borate glasses must be used since sodium reduces SiO₂.

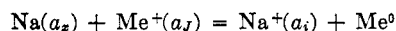


The glass merely acts as a conductor and the electrode reaction is $\text{Na} = \text{Na}^+(a_i) + e^-$; *i.e.*, the electrode is reversible to sodium ion at activity a_i in the melt and $E_{Na} = \text{constant} + RT/F \ln a_i$. The electrode is reversible to Na⁺ at concentrations as low as 0.01%.

The drawbacks of the pure sodium electrode have led to the development of alloy electrodes, particularly with Hg (17, 18, 79) and Sn (18, 33, 43). Electrodes of this type can be used to determine the potentials of various electrodes with respect to the sodium electrode as in the cell



for which the cell reaction is



and

$$E = E^\circ_{\text{cell}} - \frac{RT}{F} \ln \frac{a_i}{a_r a_x} \quad (\text{Eq 28})$$

a_x , the activity of sodium in the amalgam, can be determined from a separate set of measurements on the cell $(\text{Na} + \text{Hg})|\text{glass}|\text{Na}$. Since a_i can be very small, only a very short extrapolation is needed to give the $E^\circ_{\text{Me}/\text{MeX}}$ value. For further applications ref 1 and 19a should be consulted. Since the vapor pressure of Hg over its alloys with sodium rises rapidly with temperature, the upper limit of the Na-Hg electrode is 300°. The Na-Sn electrode in Pyrex can be used up to 700°. At higher temperatures fused silica should be used (19). Its conductivity is usually sufficient at high temperatures to permit measurement, or the glass may be conditioned by immersion in NaNO_3 at 500° prior to construction of the electrode. Pb-Na electrodes (30) have some advantages over Sn-Na electrodes. Their temperature coefficient of emf is very small, and the alloy does not expand sufficiently on freezing to shatter the glass.

B. ELECTRODE REACTIONS NOT INVOLVING SODIUM

In this type of electrode a metal and a molten salt having a common ion are contained in the glass envelope. Charge is transported through the glass by mobile ions such as sodium or lithium. All designs published so far (1) have used the Ag-Ag⁺ equilibrium, electrodes differing chiefly in the anion, the other cation(s) (generally alkali metals), and the kind of glass or ceramic.

Electrodes of this type may be used in two ways: (a) as a stable reference with respect to which emf changes due to events at the other electrode may be measured, and (b) in a concentration cell. In the former case the electrode may still be used to obtain thermodynamic data, either by calibrating it against a reference electrode having thermodynamic significance, *e.g.*, the standard Cl_2 electrode in chloride melts, or in an arrangement which does not require E° for the cell to be known. In the latter case, possible applications are similar to those for the electrodes discussed in the next section.

The treatment of concentration cells is based on Eq 23. When melts on both sides of the glass are very

dilute in silver, $a_1 \approx a_2$ and the emf is essentially that of a concentration cell (9). It is not necessary that a pure sodium salt be used. The melt must only contain sufficient sodium on both sides of the glass to ensure that sodium is the only current-carrying species in the glass. Two per cent of a sodium salt is sufficient for this (85). In principle this limitation could be removed by making glasses in which all transport occurred by some other ion, but this difficult problem has not yet been solved successfully in the general case. At lower temperatures asymmetry potentials can become appreciable (37) and the glass must be annealed. At higher temperatures the lower volatility of sulfates has some advantages over halides, in that their stability and life are increased (16). The electrodes should also be sealed to prevent vaporization of salts if they are going to be used for long periods of time. It has proved possible to use silver electrodes above the melting point of the metal (960°) by suspending a platinum wire above a melt containing Ag_2SO_4 and depending on the electrical conductivity of the gas phase. Up to 1300° potentials could be measured to within 25 mv (16). Glass membrane electrodes in concentration cells appear to be particularly convenient for measuring composition of molten salts. In order to apply Eq 23 for this purpose it was found convenient (84) to rewrite Eq 23 in terms of the mole fractions

$$E = (RT/F)t' \ln [(x_2/x_1)(x_1'/x_2')] \quad (\text{Eq 29})$$

where

$$t' = t_{\text{Na}^+} \left\{ 1 + \frac{\ln [(\gamma_2/\gamma_1)(\gamma_1'/\gamma_2')]}{\ln [(x_2/x_1)(x_1'/x_2')]} \right\} \quad (\text{Eq 30})$$

In Ag-Na systems with Cl^- , Br^- , and SO_4^{2-} anions, t' was found to be a constant equal to 1.148, 1.009, and 0.965, respectively. If the concentration on one side of the glass is the reference ($x_1 = x_r$) the unknown concentration can be calculated

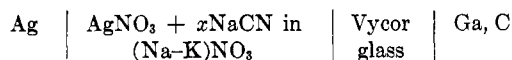
$$\log \frac{x_2}{1 - x_2} = \frac{E}{2.303(RT/F)t'} - \log \frac{(1 - x_r)}{x_r} \quad (\text{Eq 31})$$

In principle this method can be used to measure the concentration of any ion for which a reversible electrode can be constructed, but no such studies have been reported.

C. GLASS ELECTRODES WITH UNKNOWN ELECTRODE REACTIONS

In order to have a stable glass electrode it is apparently not necessary that a reversible electrode reaction occur within it, but only that the glass be equilibrated with the melt in which it is to be used. Harrington and Tien (32a, 97a-c) have described several electrodes of this type. For example, the Nernst equation was obeyed by the cell reference $(\text{Li-K})\text{NO}_3, \text{CoCl}_2|\text{Co}$ with respect to the concentration of CoCl_2 when the refer-

ence contained, variously, CoCl_2 in $(\text{Li-K})\text{NO}_3$ eutectic, $(\text{Co} + \text{Hg})$, and Hg alone, with either platinum or wolfram electrodes; *i.e.*, the cell emf was $E = E' - (RT/nF) \log [\text{CoCl}_2]$, but E' varied with the particular reference used. If the electrodes were not "aged" in the melt, emf values were time dependent, showing that ion-exchange equilibria must be established across the glass-melt interface for the "electrode function" to develop. Details of this process are still not thoroughly understood. These electrodes have proved useful in potentiometric titrations (97b) and in the determination of complex constants (97c). As an example of the latter, the complex constants for the formation of AgCN and $\text{Ag}(\text{CN})_2^-$ were determined in equimolar $(\text{Na-K})\text{NO}_3$ melt at 250° , using the cell



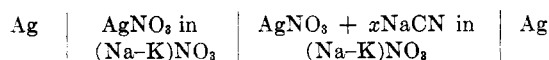
The emf of this cell is

$$E_1 = E' - (RT/F) \ln C_{\text{Ag}^+}$$

and in the absence of cyanide

$$E_2 = E' - RT/F \ln [\text{Ag}^+]$$

Hence $\Delta E = E_2 - E_1$ is the emf change of the hypothetical cell



for which

$$\Delta E = (-RT/F) \ln C_{\text{Ag}^+}/[\text{Ag}^+]$$

so that E' does not need to be known provided it remains constant.

IX. CONCLUSIONS

As a result of recent studies, the interactions between ions and the silicate network of the glass structure appear to be rather more complex than was previously thought. It is becoming clear that not only the overall chemical composition of the glass but also its detailed molecular structure affect the transport of ions in the glass. Thus the number of parameters necessary to describe the "state of the system"—method of preparation, impurity concentrations, structure defects, thermal history, etc.—has grown distressingly large. Moreover, all of these may change when the glass is used in a molten salt environment. For any particular application not all of these parameters may be significant, but the knowledge needed to make *a priori* decisions in these matters is as yet largely unavailable.

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