The glass/electrolyte solution interface

Stein, H.N.

Published in:
Advances in Colloid and Interface Science

DOI:
10.1016/0001-8686(79)80004-4

Published: 01/01/1979

Citation for published version (APA):
THE GLASS/ELECTROLYTE SOLUTION INTERFACE

H.N. STEIN
Laboratory of General Chemistry, Technological University, Eindhoven, The Netherlands

CONTENTS
I. Introduction: Some elements of glass science ................................................. 67
II. The electrolyte solution surrounding the glass ................................................. 73
III. A model of the glass/electrolyte solution interface, and the most important methods of investigation .................................................. 75
IV. Dependence on glass composition ........................................................................ 83
V. Influence of some special agents in the electrolyte solution .............................. 89
VI. Can a glass surface, in contact with an electrolyte solution, have a structure reminiscent of that of the bulk glass? ............................... 90
VII. Influence of pores ................................................................................................ 92
VIII. Some applications ............................................................................................... 93
A. Use of porous glass as a membrane ................................................................. 93
B. Origin of glass electrode potentials ................................................................. 95
References .................................................................................................................. 97

ABSTRACT
A hydrated layer is formed on most glass/electrolyte solution interfaces. Arguments for the existence of such a layer are discussed, and concentration profiles of some ions are presented. In some cases (SiO₂ glass after short contact with water at room temperature; vitreous CaSiO₃) a hydrated layer does not exist. These results are applied to the concepts of the origin of glass electrode potentials.

I. INTRODUCTION: SOME ELEMENTS OF GLASS SCIENCE
Perhaps the factor which most disturbs the understanding of phenomena concerning glasses is that quite a large number of chemists, when they come to think about it, tend to regard "glass" as one well defined substance, identical with the usual soda-lime silica or sodium borosilicate glasses met mostly in practice. Though this view may in many cases be applied without much danger, it will become apparent in what follows that it is an oversimplification which can lead to erroneous conclusions.
A glass is, by definition (ref. 1), a solid material originating from an undercooled liquid by a transition resembling a higher order phase transition. On an atomic level, glasses are characterized by the absence of long range order, while the short range order is similar to the one in the crystalline state. The difference between a glass and an undercooled liquid is that the latter is in a thermodynamic sense in internal equilibrium (though this state be metastable), whereas a glass is not (ref. 2).

Oxide glasses, which comprise the majority of all glasses known, form a structure with short range order and without long range order through a continuous network of polyhedral units, in which "glass forming" cations (e.g., Si$^{4+}$, B$^{3+}$, P$^{5+}$) are surrounded by oxygen ions† in much the same way in which they are surrounded in crystalline materials (forming SiO$_4^-$, B$_3$O$_5^-$, and PO$_4^-$ units, respectively). These units are mutually connected by Si-O-Si and similar bridges, again analogous to the situation in some types of crystals, but in glasses the mutual arrangement between these units lacks regularity. Thus, a network of mutually connected SiO$_4^-$, B$_3$O$_5^-$ or PO$_4^-$ units is formed.

In the so-called pure oxide glasses (SiO$_2$, B$_2$O$_3$, P$_2$O$_5$) the network is neutral: although, e.g., one SiO$_4$ tetrahedron would in itself not be neutral, the tetrahedra are connected by sharing oxygen ions in such a way as to make the overall composition SiO$_2$, which is neutral; see Figure 1. However most glasses contain, in addition to the glass-forming cations, other cations whose oxides are (at least, under circumstances easily attainable) unable to form glasses when pure; these oxides can form glasses, however, when combined with one or more of the renowned "glass forming oxides". Such cations (e.g., Na$^+$, Li$^+$, Ca$^{2+}$) are called "modifying". Other ions act as modifying cations under some circumstances, but as glass-forming cations in other cases. Examples are Mg$^{2+}$ and Al$^{3+}$: both act as modifying cations when present in a coordination state resembling the octahedral coordination in some crystalline compounds (e.g., MgO), but act as glass-forming cations when present in a tetrahedral type of surrounding (as, e.g., Mg$^{2+}$ in spinel, Al$_2$MgO$_4$).

In this case, the cation is called "intermediate".

A rather special type of coordination change, of great importance in glass science, is shown by B$^{3+}$. In B$_2$O$_3$, the boron is surrounded by three oxygen ions; on building some Na$_2$O (up to about 15 mole %) into the glass, an increasing number of B$^{3+}$ become surrounded by 4 oxygen ions (formation of BO$_4$ tetrahedra).

Since the network is envisaged to comprise the glass-forming cations and oxygen ions only, it carries an overall negative charge in glasses which contain modifying cations (e.g., a glass of composition Na$_2$O·4SiO$_2$). The modifying cations are thought to fit in between the network units such as to make the whole system

†For brevity, the atomic units present in a glass will be indicated throughout this review as ions (Si$^{4+}$, O$^{2-}$), although it is realized that the chemical bond is in many cases only partially of an electrostatic character.
The formation of the network in a Na\textsubscript{2}O-4SiO\textsubscript{2} glass on melting together SiO\textsubscript{2} and Na\textsubscript{2}O (or Na\textsubscript{2}CO\textsubscript{3} decomposing into Na\textsubscript{2}O and CO\textsubscript{2}) can be schematically represented as the process:

\[ \text{Si-O-Si}^{-} + \text{Na}_{2}O \rightarrow \text{Si-O}^{+} \text{Na}^{+} \text{O-Si}^{-} \]

thus, Si-O-Si bridges are broken up, and "non-bridging" oxygen ions are formed; with increasing alkali oxide content, the network is becoming "looser" or "more open", which is found to produce, for example, an increasing thermal expansion, a decreasing viscosity at equal temperature, etc. with increasing amounts of alkali oxide in the glass. An exception to this rule may occur when the glass contains appreciable amounts of B\textsubscript{2}O\textsubscript{3}; then the formation of B\textsubscript{4} tetrahedra causes the network to become more "coherent" with increasing alkali oxide content of the glass, which is found back in a decreasing thermal expansion, etc., at least at small Na\textsubscript{2}O/B\textsubscript{2}O\textsubscript{3} molar ratios. This effect is called the "boric acid anomaly" (ref. 1).

There exists a type of glass in which part of the conventional network-modifying
ions take network-forming positions. Such so-called "invert" glasses have a relatively low content of conventional network-forming oxides, but the tendency to crystallize upon cooling is suppressed by employing a mixture of other oxides (ref. 4). A typical invert glass has, e.g., the composition 12 Na₂O·12 K₂O·12 CaO·12 SrO·12 BaO·40 SiO₂. The composition appears to be quite critical for a glass 10 Na₂O·10 K₂O·10 CaO·10 SrO·10 BaO·50 SiO₂ contains enough SiO₂ to be regarded as a conventional glass, as evidenced by such properties as electric conductivity, etc.

In many glasses there exists a tendency for micro-heterogeneity, in the sense that on an atomic scale regions with a structure resembling one of the possible crystal structures are alternated by regions which are either completely disordered or which have a different structure (Figure 3). Though this question is, in the field of glass science, much debated, the answer is only of immediate importance for phenomena at glass/electrolyte solution interfaces if the heterogeneity becomes so pronounced as to lead to regions which may be regarded as separate phases.

The point in question can be illustrated most clearly by reference to some electron micrographs obtained by Spit and de Jong (ref. 5); see Figure 4. When a glass (i.e., a sodium borosilicate glass) showing a tendency towards phase separation is subjected to heat treatment, separation into two phases consisting mainly
Fig. 3. Schematic, two-dimensional representation of a glass structure in which small ordered regions are alternated by disordered regions. After Porai-Koshits (ref. 3).

Fig. 4. Electron micrograph of a Pt-C replica of an etched fracture surface of a glass, showing tendency for phase separation (5% Na₂O, 28% B₂O₃, 67% SiO₂): a. directly after manufacture; b. after heating for 1 hour at 600°C; c. after heating for 16 hours at 600°C. Etching: 1 minute, 5% HCl (ref. 5).

of sodium borate and SiO₂, respectively, will be stimulated. After treatment with acid, the sodium borate rich phase will dissolve. The resulting glass surface will consist of the other phase and contain pores, whose size will depend on the
composition of the glass and the degree of phase separation which has been allowed to occur. In such cases, diffusion processes in the pores will be important with regard to the behavior of the glass in contact with an electrolyte solution. In other cases, however (such as shown in Fig. 5), though some granularity of the glass surface is seen, there are no distinct pores on a higher than atomic level. Diffusion in pores will not be important for the processes occurring near the glass/electrolyte solution interface, and the processes taking place in the glass may be treated as occurring in a homogeneous substance. Needless to say, reality will in some cases lie in between these extremes.

The present review is concerned with phenomena occurring at room (or lower, or slightly higher) temperatures. At much higher temperatures, phenomena occurring near interfaces between glasses and molten electrolytes have been investigated intensively, with a view of application in increasing the strength of the glass (for reviews, see ref. 6 and 7). Although such systems might have been included in the present survey, if the concept of "electrolyte solution" is stretched so far as to include mixtures of molten electrolytes, this inclusion will not be made here. Under the conditions prevailing at glass/molten electrolyte interfaces, the viscosity and diffusion characteristics of glasses differ to such a degree from those found at room temperature that this subject is felt to be a separate subject apart, which should be covered elsewhere.

No attempt will be made here to present an exhaustive enumeration of all investigations carried out in the field concerned. Rather, a model for the glass/electrolyte solution interface will be developed based on some recent investigations. We will start, after some remarks on the electrolyte medium surrounding the glass...
(Section II), by considering glass surfaces which may be regarded as homogeneous
(Sections III through VI), making allowance for effects of pores in Section VII.
Finally, in Section VIII some applications of the ideas developed in previous sec-
tions will be indicated. Again, no all-comprising enumeration of all applications
should be expected since this is virtually unattainable within the limits of this
review.

Essential in any case for the understanding of glass surface phenomea is the
distinction between the network and the modifying cations. Although the bond ener-
gies between an oxygen ion and a network forming cation on the one hand, or a
modifying cation on the other arc of the same order, the former is, by reason of
its more covalent character, much less "elastic" than the latter. For practical
purposes, then, the network can be regarded as a much more stable element in the
glass structure than the position of the modifying cations.

In the following, the behavior of the surface of a vitreous material will be
considered in terms of the chemical composition of the glass. It should be kept
in mind, however, that the composition of a glass surface may differ significantly.
from that of the bulk material: some oxides used extensively in glass manufacture
(Na₂O, B₂O₃) are noticeably volatile under glass manufacture conditions, which
leads to an impoverishment of the surface with regard to these oxides and conse-
quently to an enrichment with regard to the remainder (mostly SiO₂).

II. THE ELECTROLYTE SOLUTION SURROUNDING THE GLASS

At present, there is no unanimity of opinion about the question of how far the
influence of the structure of a solid phase may make itself felt within the elec-
trolyte solution. Two types of influence are expected: a) electrical forces on
the ions in the liquid phase, and b) hydrodynamic forces through the solvent mole-
cules.

With regard to the latter, it is an established fact (ref. 8,9) that the first
layer of solvent molecules adheres strictly to the solid wall, and that movement
of liquid versus the solid phase becomes possible only at some distance from the
solid wall, in the so-called "electrokinetic shear plane" or "slipping plane"
(ref. 10). But opinions differ in regard to the exact location of the position
of the slipping plane: whereas most authors (ref. 11,12) place it at a distance
of a few tenths of a nanometer (a few Ångström units) from the phase boundary,
others (ref. 13-16) find arguments for believing in a stagnant layer of hundreds
of molecules thick. It would lead us too far astray to treat this subject in de-
tail; the arguments pro and con have been reviewed recently (ref. 17-19). The
main pro arguments are: 1) On heating, thermal anomalies are observed in systems
with a solid-liquid interface. These anomalies are ascribed to structural changes
in the "interfacial water"; 2) continued washing of a precipitate leads to changes
in the composition of the liquid. These changes are interpreted as indicating
that during the first washings some liquid remains stagnant near the phase boundary and is only in the long run replaced.

However, these arguments have been doubted (ref. 18,20), and the point appears at present not to be settled. An important objection against a stagnant layer of appreciable thickness is the close relationship between the $\zeta$ potential and the outer Helmholtz plane potential $\psi_d$ as calculated from coagulation (ref. 18). If a stagnant layer of some hundred molecules thick really exists, then the vitreous nature of a solid phase should make itself felt quite distinctly: for a crystalline solid whose structure resembles that of ice, the electrokinetic slipping plane should then be located significantly farther away from the phase boundary than for a solid of equal composition but with disordered structure. This difference should lead to a distinct difference in, e.g., $\zeta$ vs. pH curves. For $\text{SiO}_2$, no significant differences in $\zeta$ vs. pH curves between a crystalline and vitreous solid are observed (ref. 21); see Fig. 6. Differences in $\zeta$ vs. log $[\text{CaCl}_2]$ curves have been observed for vitreous and crystalline calcium silicates (see Section VI) (ref. 22) but these differences consist in a shift of the IEP rather than in a difference in absolute values of the $\zeta$ potential, as expected if there would be significant differences in stagnant layer thickness.

In view of the fact that ordering between water molecules does not, in the bulk water, extend over hundreds or thousands of Ångström units (non-existence of "poly-water"), an extensive ordering near an interface appears to be unlikely. The non-electrostatic forces acted on water molecules by the wall become negligibly small at distances larger than a few Ångströms; any ordering tendency experienced by a

![Fig. 6. $\zeta$ potential vs. pH for various solids. $10^{-3}$ M NaCl background electrolyte (ref. 21).](image-url)
water molecule at a distance of say 20 Ångström units can then only be due to interaction with water molecules placed between the wall and the water molecule concerned. However, this interaction does not, in the bulk water, lead to such large aggregates.

On the other hand, at present sufficient data are not available to warrant identification of the potential at the outer Helmholtz plane and the ζ potential. A definite elucidation of this point would increase significantly the usefulness of the ζ potential.

The electrical forces acted on the ions in the liquid by the solid are much better known, at least under conditions where the ions may with reasonable accuracy be treated as point charges, such as to make the Gouy-Chapman theory applicable. The innermost part of the double layer (between the phase boundary and the slipping plane), however, again is not easily accessible for theoretical considerations in view of uncertainties with regard to local potentials, dielectric constant, etc.

III. A MODEL OF THE GLASS/ELECTROLYTE SOLUTION INTERFACE, AND THE MOST IMPORTANT METHODS OF INVESTIGATION

When a glass is situated in an electrolyte solution, the first thing to be expected is "adsorption" of ions unto the glass surface, or desorption from it. A well-known case is that of aluminum ions (ref. 23) effecting a charge reversal on a Pyrex glass surface: the net charge behind the electrokinetic slipping plane is, in the absence of aluminum ions, negative at the pH concerned but becomes positive through adsorption of cations. The total potential drop over the surface, however, is not noticeably influenced by aluminum ions. Figure 7 depicts the potential as a function of the distance from the wall, considered as an explanation of these observations. More recent observations (ref. 24) indicate more complex ions such as \( \text{Al}_8\text{(OH)}_{10}\text{(SO}_4\text{)}_5^{4+} \) as responsible for the charge reversal in a similar case (pH: 5.4-6).

It is, however, an oversimplification to regard the glass surface as merely an inert substrate for adsorption. A more or less inert character of glass as a substrate for adsorption is certainly to be expected if the solute adsorbed is bound by hydrogen bonds to the surface (e.g., proteins [ref. 25]). Toward ions on the other hand, oxide glasses often behave in a more complicated way: the adsorption of one ion onto the glass is frequently accompanied by desorption of another ion. It often depends on the conditions of the experiment, in particular on the kind of ion present in the solution as to whether one should speak about adsorption or about ion exchange.

If there are neutral molecules present in the solution (e.g., \( \text{HgCl}_2 \), \( \text{Hg(OH)}_2 \) in \( \text{Hg}^{2+} \) containing solutions), then real adsorption is expected. An argument in this case is the absence of influence of indifferent electrolytes such as \( \text{NaNO}_3 \) on the adsorption (ref. 26) (an ion exchange type of sorption should be suppressed
by the addition of indifferent electrolytes), whereas NaCl addition influences the sorption in a way compatible with HgCl₂ formation. The presence of mercury in the solution as neutral molecules could be confirmed by the absence of sedimentation in a centrifugal force field and the absence of migration in an electric field (ref. 27). In the case of Hf, adsorption of neutral Hf(OH)₄ forming a monolayer on glass has been reported (ref. 28-30). This adsorption has been suggested as a convenient way to measure surface areas since the Hf(OH)₄ molecules are strongly adsorbed and formation of a close-packed monolayer is facilitated by the absence of lateral repulsion between the adsorbed species. The evidence, however, has been questioned (ref. 31) because of the difficulty in obtaining equilibrium in Hf⁴⁺ containing solutions; other investigators obtained Hf(OH)₄ removal from the solution by glass only, when precipitation of Hf(OH)₄ occurred. In itself, a (nearly) electroneutral composition of a surface cover cannot be accepted as evidence for "surface precipitation", as will be treated in Section VI.

Removal of Ag⁺ ions by glass from the surrounding electrolyte solution is influenced in the way to be expected for ion exchange (ref. 32,33): NaN₃ addition suppresses the sorption of Ag⁺ to a borosilicate glass in the same way as a pH change from 8 to 6; this can be interpreted as a competition between Ag⁺, H⁺ and
Na⁺ for adsorption sites on the glass surface. In other cases (Fe³⁺ [ref. 34], Eu³⁺ [ref. 35], Y³⁺ [ref. 36]) either adsorption or ion exchange is observed, depending upon the pH of the solution. In some cases, ions are removed by glass even from very dilute (≈10⁻⁹ M solutions [ref. 36]). This finding should be a warning against employing glass vessels for storage of solutions in which very small concentrations are important such as may be encountered, e.g., in geochemical work.

Ion exchange on porous alkali borosilicate glasses (prepared by phase separation and extraction of a ternary Na₂O·B₂O₃·SiO₂ glass, see Section VII) is restricted in the main to singly charged cations (ref. 37). These cations have a coefficient of ion exchange selectivity decreasing in the series Tl⁺ > Ag⁺ > K⁺ > Na⁺ > Li⁺. The ion exchange appears to be related in these glasses to the presence of B-OH groups in narrow pores. For higher charged cations, ion exchange is found to be slight and is restricted to neighboring B-OH groups. Moreover, the sorption of higher charged cations frequently leads to a change in structure of the porous glass. On a glass of more complicated composition, ion exchange has been observed for Ba²⁺ but this adsorption has an irreversible character (ref. 38), only part of the barium being recovered on subsequent treatment with H₂O. Thus, a glass surface may behave in a more complicated way than corresponds with either adsorption or ion exchange or both.

More precise arguments for this statement are found by considering the kinetics of the uptake of ions by, or their liberation from, the glass. Moiseev and Plotnikova (ref. 39) argue that when a film unaltered, with the exception of ion exchange, would originate on the surface of the glass, the diffusion rate of ions given off by the glass through this film should be determined by the slowest step, i.e., bulk diffusion of the ions through the glass towards the surface. Early investigations (ref. 40) indeed suggest a similar diffusion coefficient for Na⁺ on extraction of a glass as found for bulk diffusion. However, later investigations covering a more extended range of glass compositions show that the diffusion coefficient describing the extraction process is larger than that describing bulk diffusion. Moiseev and Plotnikova, too, found that the diffusion coefficient of Na⁺ ions in Na-aluminosilicate glasses (ref. 39) describing the leaching-out process differs by three orders of magnitude from the bulk diffusion coefficient, the latter being the smaller one. This discrepancy is ascribed to the formation of a hydrated, "swollen" film on the glass surface, in which diffusion of Na⁺ is considerably faster than in the bulk glass.

A direct confirmation of this idea is given by the measurement of diffusion coefficients in the surface layer and in the bulk by tracer experiments (ref. 42), showing indeed a much faster transport of ions in the surface layer than in the glass, and quite different ratios of diffusion coefficients for surface layer and bulk: whereas, for instance, in the bulk glass D_{Na}/D_{K} is about 1000, it is
only 5 to 10 in the surface layer.

This discrepancy between bulk and surface layer ion transport in soda-lime silica glasses has been accounted for by considering that in the bulk not all Na\(^+\) ions present participate in the ion transport process, but a small fraction only. Thus, when for the concentration of ions participating in the bulk diffusion, the "electrolytic concentration" is filled in, the discrepancy vanishes (ref. 43). This electrolytic concentration \(Z\) is calculated from the electrical conductivity \(c\), by the relation:

\[
c = 2 \, Z \, e_0 \, 1 \, v \, \exp \left( -\frac{U}{kT} \right) \sinh \left( e_0 \, E \, l/2kT \right), \tag{1}
\]

where

- \(e_0\) = elementary charge
- \(l\) = jump distance of a cation
- \(v\) = frequency of a lattice vibration
- \(U\) = empirical (free) activation energy of the conductivity
- \(E\) = electrical field strength.

This equation can be derived from a simple model for the conduction process when the transport number for the cations concerned is equal to 1. In essence, use of this relation implies that the diffusion and conduction processes in the bulk glass are lowered in the same proportion in comparison with the processes in the surface layer. The "overall" diffusion constant should be distinguished from a "true" diffusion coefficient, related to that fraction of the ions which are free to move.

However, Doremus (ref. 44) recently stresses that ionic transport processes in the surface layer of glasses are determined to a large extent by the fact that we are dealing here with interdiffusion of two ions rather than with diffusion. As experimental evidence in this respect, an investigation by Scholze (ref. 45) can be referred to. Scholze could describe the leaching of Na\(^+\) ions from a glass as a process where Na\(^+\) ions diffuse through a hydrated layer to the outside, and H\(^+\) ions diffuse toward the interior. When two ions, such as Na\(^+\) and H\(^+\), which in themselves have different transport rates, are exchanged, a potential difference will originate which will slow down the faster ion and speed up the slower one, until they have the same transport rate. For every species, the transport can be described by an "interdiffusion constant":

\[
D_{\text{interdiff}} = \frac{D_A D_B}{c \, D_A + (1-c) \, D_B}, \tag{2}
\]

where \(c\) = the fraction of species A of all ionic species present.

It is important that this interdiffusion "constant" is strongly concentration dependent.

That diffusion of alkali ions in a surface layer is the rate determining step
in the transport of ions from the glass to the outside follows also from the fact that an interruption in an extraction experiment leads to a higher leaching rate shortly after contact with the electrolyte solution is resumed (ref. 46). The interruption apparently gives the alkali ions the opportunity to sweep out concentration gradients in the hydrated layer.

On close inspection (ref. 47-50), however, this model for the processes at the glass/electrolyte solution interface falls short of reality for at least some glasses: the leaching process starts all right, with the amount extracted increasing proportional to the square root of the time. This rate indeed would be expected for a process controlled by diffusion through a surface layer formed during the process itself, yet finally it frequently becomes proportional to the time. In this later stage, the hydrated layer has a constant depth, and is dissolved at its outside with the same rate as its inner front advances into the bulk glass. Figure 8 shows some typical results obtained with a glass composed of 15 Na₂O-5 Al₂O₃·80 SiO₂.

![Fig. 8. Quantities of Na₂O and SiO₂, extracted from a glass 15 Na₂O·5 Al₂O₃·80 SiO₂ on treating with water at various temperatures, plotted against time and $\sqrt{t}$ (ref. 48).](image-url)
The relative ease with which the network remaining after an exchange of Na\(^+\) against H\(^+\) is dissolved is thought to be due to stresses induced by the ion exchange (ref. 50). The correctness of ascribing the transition of a \(\sqrt{t}\) proportionality of the amount extracted to a constant extraction rate, to dissolution of the hydrated layer, has been confirmed both by measurement of the amount of network-forming oxide passing into the solution (ref. 47,48) and by the observation that sodium borate glasses, where dissolution of the network is much faster than with silicate glasses, show a constant extraction rate from the beginning (ref. 51).

For other glasses, a \(\sqrt{t}\) proportionality is found at low pH and a constant extraction rate at high pH, the transition being at pH 10-10.5 (ref. 52). This change also corroborates the proposed mechanism, indicating (inter)diffusion as rate determining step at lower pH and dissolution of the remaining network at higher pH. The dissolution of the network is catalyzed by OH\(^-\) ions (ref. 48). This pH effect means that care must be exercised to keep the pH constant, when either the kinetics of the process are determined, or the kinetic data are applied to practical situations. If the pH is not kept constant, changes in it caused by the reaction of the glass with the electrolyte solution will affect the reaction rate (ref. 53). Starting from neutral solution, the pH increases by the reaction with the solution for most glasses. Starting from alkaline solutions, the pH decreases. In some cases (ref. 54,55), an "equilibrium pH" has been determined (i.e., a pH which does not change on continued extraction). Characteristic values are 10.9 and 11.8 for alkali oxide-CaO-SiO\(_2\) glasses.

We have at our disposal some concentration profiles in the hydrated layer. Figure 9 shows the Na\(^+\) concentration found in successive layers etched away from

![Fig. 9. Na\(^+\) concentration as a function of depth in some glass/electrolyte solution surface layers (ref. 47); $\Delta = 28$ Na\(_2\)O. 4 BaO. 68 SiO\(_2\), leached for 144 hours at 40\(^\circ\)C; $+$ = 28 Na\(_2\)O. 4 SrO. 68 SiO\(_2\), leached for 144 hours at 40\(^\circ\)C; $\circ = 20$ Na\(_2\)O. 12 SrO. 68 SiO\(_2\), leached for 288 hours at 40\(^\circ\)C.](image)
the surface of Na$_2$O-BaO-SiO$_2$ and Na$_2$O-SrO-SiO$_2$ glasses after exposure to water at 40°C (ref. 46) (thus, the "g. atom of silica" plotted on the horizontal axis is a quantity proportional to the depth of the etching). Figure 10 gives a similar graph for a 20 K$_2$O. 12 SrO. 68 SiO$_2$ glass.

![Graph](image)

Fig. 10. K$^+$ concentration as a function of depth in the surface layer of a 20 K$_2$O. 12 SrO. 68 SiO$_2$ glass leached in water at 40°C (ref. 47).

Perhaps the most striking thing about these graphs is the different character of the concentration profile in the hydrated layer of Na and K glasses. This difference has been explained (ref. 56) as follows: When Na$^+$ is exchanged against H$^+$ and the concentration of the sodium ions passes a certain critical limit, the network undergoes a distinct change resulting in a looser structure: H$_2$O molecules run along with H$^+$, and H$_3$O$^+$ ions require more space than the Na$^+$ ions originally present. As a consequence, the diffusion coefficient in the hydrated layer is for Na$^+$ higher than in the bulk glass. For K$^+$ ions, having a size nearly equal to that of H$_3$O$^+$ ions, this effect is absent. Similarly, a loose "swollen" layer is absent when the glass had been in contact with ethanol containing only minor amounts of water (ref. 56). Similar phenomena have been reported (ref. 57) for Na$_2$O-K$_2$O-SiO$_2$ glasses; whereas the K$_2$O/SiO$_2$ molar ratio in the extract is equal to that in the bulk glass, the Na$_2$O/SiO$_2$ molar ratio is not. It should be noted, however, that this explanation is not in agreement with Eisenman's data (ref. 42) on diffusion coefficients since these indicate that the large difference in transport rates of Na$^+$ and K$^+$ is lessened in the hydrated surface layer. Perhaps the difference in composition between the glasses investigated by the different groups is responsible for this discrepancy.

A quantitative description of such concentration profiles can be achieved only if both the interdiffusion character of the process and the dissolution of the hydrated layer at its outside are taken into account (ref. 44). An unexpected feature is, in Na$^+$ against H$^+$ exchange, that H$^+$ transport is initially the lower
one, since the hydrogen ions are "trapped" by forming silanol groups according to:

\[ \equiv \text{Si} - \text{O}^{-} + \text{Na}^{+} + \text{H}^{+} \rightarrow \equiv \text{Si} - \text{OH} + \text{Na}^{+}. \]

Recently, significant contributions to our knowledge of concentration profiles in the surface layer of glasses have been obtained through application of electron microprobe analysis (ref. 58) and Auger electron spectroscopy (ref. 59). In applying the latter method, special care has to be taken to prevent migration of adsorbed and mobile species over the surface. Results will be treated in Section IV.

In some cases (ref. 60,61), data have been obtained for the water content of the surface layer as a function of increasing depth. Fig. 11 shows results (ref. 61) obtained by IR absorption, after etching with HF for different periods, concerning the surface layer of a 20 Na_{2}O. 6 CaO. 74 SiO_{2} glass exposed for 4 days at 60°C in a HCl solution (pH = 1.6). The IR absorption densities at \( \lambda = 6.2 \ \mu\text{m} \) and at \( \lambda = 2.9 \ \mu\text{m} \) (corresponding to molecular H_{2}O and SiOH groups + molecular H_{2}O, respectively) have been plotted in Fig. 11, as well as the concentrations of the species concerned derived from the IR absorption (the concentrations are represented by the dotted curves). It is seen that under these conditions the hydrated layer extends for about 1-3 \( \mu\text{m} \) into the glass.

![Concentration of molecular H_{2}O and SiOH groups as a function of depth](image-url)
Within the hydrated layer, an ion exchange equilibrium exists between alkali ions and $H^+$ (or $H_3O^+$) ions, as shown by the linear dependence of the logarithm of the residual alkali ion concentration on the pH of the surrounding medium (ref. 62,63).

Dobos (ref. 64) distinguishes two regions in the hydrated layer of a 24 Na$_2$O.4 BaO. 68 SiO$_2$ glass: a more dense, inner one (where $H^+$ ions can migrate, but $H_3O^+$ cannot), and a more loose, outer one wherein $H_3O^+$ ions can migrate as well. In the latter, the $H_2O$ content increases toward the leached layer/electrolyte solution interface; and alkali ions in it are in the fully hydrated state. In this outer layer, 3-4 moles of water are found per mole of Si. Since this ratio is incompatible with a continuous network, it follows that this part of the surface layer is heterogeneous, consisting of a $H_2O$-rich, liquid phase intermingled with a SiO$_2$-rich, solid phase, both finely divided. In view of the pronounced dependence of phase separation on glass composition and treatment (see Section VII), this situation will be different for different types of glasses, so no general conclusion can be drawn from Dobos' results.

More indirect information on the surface layers formed by treating the glasses with aqueous solutions is obtained by studying electrical surface conductivity of a leached glass after drying, e.g., as a function of relative humidity. Although this property is determined primarily by the surface layer concerned, its interpretation is not always certain. In some cases, for instance, it is assumed that $H^+$ ions are primarily responsible for conductance of an electrical current in the surface layer (ref. 65). This mechanism is doubtful in view of the retardation of $H^+$ ion movement in a hydrated glass by binding as silanol groups. Nevertheless, some significant results have been obtained by this method. Among them we mention the following:

1. Upon drying, cracks are produced in the outermost part of the hydrated layer. These cracks lead to suppression of electrical conduction in the outermost layer (ref. 65).
2. Rewetting by water vapor adsorption is accompanied by an increase in surface conductivity of several orders of magnitude, as soon as enough water is adsorbed to form a coherent liquid film (ref. 66).
3. At low relative humidities where such a coherent film is not formed, a constant (i.e., independent of relative humidity) surface conductivity is observed ascribed to an "interior stratum" not directly influenced by the atmosphere (ref. 67).

IV. DEPENDENCE OF GLASS COMPOSITION

In the foregoing, reference had to be made to phenomena observed with glasses of different compositions, simply because not one single glass can yield us enough information on all processes taking place. What kind of regularities can be for-
ulated with regard to the dependence of these phenomena on the composition of the glass?

The first thing to be remarked is that in general increasing quantities of alkali oxide will make a glass more sensitive toward attack by water. A more open structure of the network (characterized by larger amounts of non-bridging oxygen and alkali ions) will facilitate both the ion exchange and the diffusion of the ions in the hydrated layer formed, as well as the breaking down of the remaining network. The latter is essentially a depolymerization process of an ion of polysilicic acid. Glasses with a higher alkali oxide content have a network which in itself is already partially depolymerized to a larger extent.

Observations in this respect date back to the 19th century (ref. 68). Modern methods such as electron microprobe analysis and IR spectroscopy confirm these findings (ref. 69,70).

In binary alkali silicate glasses, a surface layer enriched in SiO_2 is formed on contact with water. The composition of this film is determined by the "degree of selectivity of glass dissolution" (ref. 71) defined, for a glass of composition Na_2O. m SiO_2, as:

\[ a = \left( \frac{N_{SiO_2}}{m} \right) \times \left( \frac{1}{N_{Na_2O}} \right), \]

where \( N \) is the amount of SiO_2 or Na_2O dissolved; \( a \) can be related to the rates of penetration of water into the bulk glass on the one hand, and of dissolution of the hydrated layer at its outside on the other (see Section III).

With borate glasses, however, the introduction of alkali oxide leads to an increased resistivity of the glass against water, at least at low alkali oxide contents, because of the coordination change of B from 3 to 4 ("boric acid anomaly").

The influence of divalent cations, counteracting the water attack, has been investigated intensively in the 1920's (ref. 72). Its mechanism can be described best by referring to Fig. 9, where Na_2O-SrO-SiO_2 glasses with equal molar SiO_2 content are compared. Substitution of Sr^{2+} for 2 Na^{+} decreases the depth of the hydrated layer considerably, but the final Na^{+} concentration is not noticeably influenced. Doremus (ref. 53) ascribes the increased durability against water, on substituting an alkaline earth oxide for an alkali oxide, to a lowering of the bulk diffusion of alkali ions in the glass by the presence of divalent ions. It seems more plausible, however, to relate the effect to diffusion characteristics in the hydrated layer and to differences in the dissolution rate of the hydrated layer at its outside.

In Na_2O-CaO-SiO_2 glasses, the diffusion coefficient describing the Na^{+} extraction is practically constant at constant Na_2O/CaO molar ratio (see Fig. 12).
Fig. 12. Loci of equal diffusion constants of Na\(^+\), on leaching glasses Na\(_2\)O-CaO-SiO\(_2\) in 0.1 N HCl at 50.2°C (ref. 45).

Thus, at constant SiO\(_2\) content, a replacement of Na\(_2\)O by CaO is accompanied by a pronounced decrease in the apparent diffusion constant of Na\(^+\); while at constant Na\(_2\)O content, a replacement of SiO\(_2\) by CaO decreases the Na\(^+\) diffusion constant as well, and is accompanied by an increased resistivity of the glass against attack. IR spectroscopy indeed shows that the vibration modes of bridging and non-bridging oxygen ions are coupled stronger if SiO\(_2\) is partially replaced by CaO; thus, the network is considerably strengthened by this substitution (ref. 73). Therefore, the simple model of bridging and non-bridging ions as determining the properties of a glass should be used with caution!

That the situation at the surfaces of Na\(_2\)O-CaO-SiO\(_2\) may be a complicated one is shown by concentration profiles. Thus, in a 20 Na\(_2\)O. 10 CaO. 70 SiO\(_2\) glass the surface layer is depleted in Na\(^+\) by treatment with water to 100°C, as expected, but the calcium concentration shows a complicated pattern (ref. 74); the outermost part of the surface layer is enriched in Ca\(^{2+}\), then follows a region poor in Ca\(^{2+}\) (about 1500 Å thick after 9 days' exposure), thereafter the Ca\(^{2+}\) concentration rises toward a maximum at a depth of about 3100 Å (see Fig. 13). This distribution is ascribed to precipitate formation, e.g., of CaSiO\(_3\), near the outermost surface (however, precipitation of a calcium silicate hydrate is more plausible).

For quaternary glasses K\(_2\)O-CaO-MgO-SiO\(_2\), it has been reported that the stability against attack by water is determined primarily by the number of non-bridging oxygen
Fig. 13. Auger signals at various depths in a 20 Na₂O. 10 CaO. 70 SiO₂ glass after 9 days' exposure to water at 100°C. Layers of increasing depth were removed from the glass surface by ion milling (rate ~ 3 nm/min⁻¹) (ref. 74).

ions (ref. 75). The rate of attack becomes small when the SiO₂ content surpasses 66 mol %. This limit cannot, however, be generalized to all such glasses; in Na₂O-CaO-SiO₂ glasses of molar Na₂O content = 15%, substituting CaO for SiO₂ makes the resistivity against water pass through a maximum at 10 mol % CaO for the diffusion controlled initial attack, and through a maximum at a slightly lower CaO content for the dissolution process (ref. 54). These findings mean that a network containing some difficultly exchangeable cations like Ca²⁺ is more resistant than a pure SiO₂ network! This result is not necessarily in disagreement with Schulze's data on the apparent diffusion constants of Na⁺ during the leaching process (see Fig. 12) because Schulze investigated only a limited composition range at Na₂O = 15 mol %. It stresses, however, the danger of extrapolating from experiments concerning a limited composition range to glasses of different compositions.

With regard to the difference between the various alkaline earth cations, the following can be noted: the data of Fig. 9 indicate a Sr²⁺ containing glass to be, ceteris paribus, slightly more resistant than a Ba²⁺ glass. Mg²⁺ has been found to be even more resistant toward being leached out, at least in alkaline media, than the silicate network (ref. 76); but it should be kept in mind that
Mg$^{2+}$ ions can be present either as parts of the network (they are small enough to be accommodated by a tetrahedron of oxygen ions) or as modifying cations. Thus, in ternary Na$_2$O-MgO-SiO$_2$ glasses of constant Na$_2$O content, substitution of SiO$_2$ by MgO leads to a lower rate of water attack up to a MgO/Na$_2$O molar ratio of about 3.5; but beyond that limit the substitution of SiO$_2$ by MgO decreases the resistivity toward water. As long as the Mg$^{2+}$ ions are accommodated into the network, substitution of SiO$_2$ by MgO increases the durability of the glass (ref. 77,78).

Invert glasses are, by reason of their distinctly "open" network structure with many non-bridging oxygen ions, rather liable toward attack by water. This sensitivity has been used for developing a special glass compatible with biological tissues, the so-called "bioglass" (weight %: 24.5 Na$_2$O, 24.5 CaO, 6 P$_2$O$_5$, 45 SiO$_2$) (ref. 79). In neutral aqueous media, a SiO$_2$-enriched surface layer develops and within it, near the surface, a film enriched in CaO and P$_2$O$_5$, probably by precipitate formation. In the case at hand, this film attains an additional importance because the calcium phosphate-rich surface film forms a strong and stable bond with bone tissue.

We owe to Hair (ref. 80) interesting data about the position of Mg$^{2+}$ and Ca$^{2+}$ ions in the hydrated layer of a Na$_2$O-CaO-MgO-SiO$_2$ glass. The preferential leaching of Na$^+$ ions leaves the Mg$^{2+}$ and Ca$^{2+}$ ions apparently in rather exalted positions, because they can, after drying, act as Lewis acid sites toward organic molecules adsorbed from the gas phase.

It is to be regretted that the extensive data collected with regard to the influence of ions of higher charge than 2 on the water attack on glasses have not yet, to the knowledge of the present author, led to an unequivocal mechanism of the processes concerned, and to a model of the situation in the hydrated layer in those cases. An example in this respect is the case of the Al$^{3+}$ ion. Its stabilizing influence on the durability of glasses has been known for quite a long time (ref. 81,82). There are arguments (ref. 53) for assuming that this is due to the decrease in the number of Na$^+$ ions that exchange with H$^+$ ions from the solution. The SiO$^-$ anionic groups are said to be more compact; their negative charge is less spread out than that of an AlO$^-$ group. This difference causes the latter to prefer large ions, the former to prefer small ions; thus, exchange of Na$^+$ for H$^+$ is counteracted by the presence of Al$^{3+}$ in the network (ref. 83). On the other hand, a decreased tendency of the strongly acid ionogenic -OAlO$^-$H$^+$ groups toward condensation, as compared with silicic acid groups, has been considered to play a role (ref. 84). Alternatively, surface "clogging" by Al(OH)$_3$ formation is suggested by the concentration profiles concerned (ref. 73,85).

In the special case of Na$_2$O-B$_2$O$_3$-SiO$_2$ glasses, the stabilizing effect of an increasing Al$_2$O$_3$ content with regard to attack by water (ref. 86) can be ascribed to an increase of the interfacial tension between SiO$_2$-rich and SiO$_2$-poor phases, counteracting the tendency for phase separation which in this case would increase
the rate of water attack (see Section VII) (ref. 53). By the same argument, how-
however, in Na$_2$O-B$_2$O$_3$-SiO$_2$ glasses of low alkali oxide content the presence of small
amounts of Al$_2$O$_3$ decreases the durability of the glass. The counteraction of
phase separation results in a homogeneous surface which is chemically less resis-
tant against water than a phase separated glass with a continuous phase of prac-
tically pure SiO$_2$ (ref. 87). Therefore, in these glasses tempering (which stim-
ulates phase separation) increases the chemical durability of the glass (ref. 88).

The influence of substitution of ZrO$_2$ for SiO$_2$ is remarkable. The resistivity
against alkaline attacks (ref. 89,90) increases. The effect is much used in prac-
tice (ref. 91). Lack of data on the composition of the hydrated surface layer,
however, causes uncertainty as to whether the strong retarding action exerted by
Zr$^{4+}$ during the leaching process should be ascribed to a strengthening of the
residual network (i.e., less easy disruption of Zr-O-Si bonds than of Si-O-Si
bonds) or to precipitation of some Zr-containing species after destruction of
the original network.

A glass of rather extreme composition, but which is used extensively, is quartz
glass or vitreous silica (nearly pure SiO$_2$). In this special case, the situation
at the glass/electrolyte solution interface can be compared with surfaces of oxides
such as crystalline SiO$_2$, TiO$_2$, Fe$_2$O$_3$, etc. For these surfaces of crystalline
oxides, it has been concluded from colloid chemical data (ref. 92) that they should
be considered to be covered by a hydrous gel layer, if only because a satisfactory
agreement between calculated and experimental diffuse layer potentials can be ob-
tained only when the surface potential $\psi_0$ is taken to be less than that given by
the Nernst equation:

$$\psi_0 = 2.303 \frac{RT}{F} (\text{pH}' - \text{pH})$$

where $\text{pH}' = \text{pH at which } \psi_0 = 0$. On the basis of a hydrated surface layer into
which counterions can penetrate, it is indeed possible (ref. 93-95) to derive satis-
factorily the $\zeta$ potential vs. log c curves found experimentally ($c = \text{indifferent}
\text{electrolyte concentration}$). However, in spite of the mathematical effort used to
obtain this result, it is very doubtful whether the model corresponds to reality
in the case of (non-porous) SiO$_2$. A hydrated surface layer may be formed in
this case, to be sure, but only by treatment at higher temperatures (ref. 96-98).
At room temperatures, for periods of about one day, no surface gel layer is devel-
oped, as shown by the lack of $^{24}\text{Na}^+$ penetration into the solid. All Na$^+$ ions ad-
sorbed onto the solid, both at pH 4 and pH 10, can be removed by etching under
conditions where 0.3 mm quartz glass is dissolved (ref. 99). Therefore, in the
case at hand, a site binding model as developed by Yates c.s. (ref. 110) is more
appropriate, and the explanation of the lack of agreement between theoretical and
experimental $\zeta$ vs. log c curves through formation of a hydrated surface gel must
be rejected.

This conclusion does not imply that the vitreous silica retains its bulk properties up to its surface. By ellipsometry, a persistent surface layer differing from the bulk glass is found even after etching in HF solution or sputter cleaning (ref. 101). However, in view of the Na\(^+\) sorption data referred to, this finding should be ascribed to stresses or defects in the surface layer rather than to complete hydration.

In practice, the ideas on the formation of a hydrated surface layer described can be employed for developing methods to protect a glass surface against corrosion. Frequently, protection by a hydrophobizing (e.g., silane type) coating cannot be applied since the glass surface must remain hydrophilic for many applications. In this case, an occupation of adsorption sites on the glass by ions may be resorted to (ref. 102), among which Be\(^{2+}\) appears to be the most effective protective agent against attack in alkaline media. The method must, however, be used intelligently; especially in acid media, protection by heavy ions cannot be expected. On the contrary, they frequently are leached out preferentially, as found, e.g., for Pb silicate glasses during treatment with acetic acid (ref. 103) at 40-60° C; the IR reflection spectrum approaches that of vitreous silica.

Other glasses than silicate glasses have only seldom been investigated with regard to their behavior toward aqueous electrolyte solutions. Mention should be made of data collected for CaO-B\(_2\)O\(_3\)-Al\(_2\)O\(_3\) glasses (ref. 104) showing that a surface layer is formed consisting for the greater part of hydrated alumina and containing still some calcium ions. This layer is less resistant toward water than the hydrated layer formed on silicate glasses, but the resistance can be brought to the same level by introducing some SiO\(_2\) into the glass. Relatively small amounts of SiO\(_4\) tetrahedra in such a network can stabilize it quite efficiently against water.

Some cases have been reported in which the network dissolves preferentially, leaving back the network-modifying cations with hydroxyl groups. Such is the case, e.g., when Li\(_2\)O-SrO-B\(_2\)O\(_3\) or K\(_2\)O-SrO-B\(_2\)O\(_3\) glasses are brought into contact with aqueous solutions; if the latter contain phosphate ions, Sr phosphate is precipitated. Since the latter's distribution on the surface reflects the spatial distribution of the ions in the original glass (ref. 105), little transport of the Sr\(^{2+}\) ions before precipitation can have occurred.

Similarly, it has been found for CaO-Ga\(_2\)O\(_3\)-SiO\(_2\) glasses (ref. 106) in alkaline media that Ga\(_2\)O\(_3\) and SiO\(_2\) are preferentially leached out, and that Ca containing salts remain.

V. INFLUENCE OF SOME SPECIAL AGENTS IN THE ELECTROLYTE SOLUTION

As special agents, which may influence processes at glass/electrolyte solution interfaces, should be mentioned: anions such as Cl\(^-\) which are expected to be indiff-
different but nevertheless have some influence; and complex forming agents such as EDTA.

With regard to the former, Dobos observed (ref. 64) that neutral chloride solutions attack glasses more heavily than solutions which do not contain Cl\(^-\) ions. Nevertheless, no Cl\(^-\) ions could be detected in the hydrated surface layer. The increased attack can therefore be ascribed to a catalysis by Cl\(^-\) in neutral or alkaline solutions of the Si-O-Si bond hydrolysis in the outermost part of the surface layers. The effect, however, appears not to be a general one; some glasses are, on the contrary, more resistant toward neutral alkali chloride solutions than toward water (ref. 107). This resistance is thought to be due to a decreased exchange of alkali ions from the glass against H\(^+\) by the presence of alkali ions in the surrounding solution. Thus, in the complicated behavior toward neutral chloride solutions, the fact is reflected that the attack of glasses by water is a multistep process including both formation of a hydrated layer and its dissolution (see Section III).

Complex forming agents decrease the activity of modifying cations in the solution (when solutions with equal concentrations of these cations with and without a complex forming agent are compared), and therefore are expected to increase the leaching rate. This increase has been observed by Olsen c.s. (ref. 108) for Pb\(^{2+}\) containing glasses, with EDTA as a complex forming agent, in hot alkaline solutions. The other constituents of the glass (K\(^+\), silicate) pass into the solution at the same rate as the Pb\(^{2+}\) ions, although they do not form complexes with EDTA. This result means that the removal of Pb\(^{2+}\) ions (i.e., their exchange against 2 H\(^+\)) weakens the silicate structure of the boundary layer such as to hasten its deterioration.

At first sight, there is a contradiction between Olsen's results and those reported by Wood and Blachère on preferential leaching of Pb\(^{2+}\) ions from silicate glasses (ref. 103). However, under the conditions for leaching employed by Olsen, dissolution of the network at its outside presumably is much faster than under the acid treatment conditions used by Wood and Blachère. Olsen's results can be considered to apply to the stationary state in which the hydrated layer dissolves at its outside with a rate equal to that at which it is formed inside the bulk glass.

VI. CAN A GLASS SURFACE, IN CONTACT WITH AN ELECTROLYTE SOLUTION, HAVE A STRUCTURE REMINISCENT OF THAT OF THE BULK GLASS?

It appears from the foregoing that glasses can undergo profound changes at their interfaces with aqueous electrolyte solutions. Are there, nevertheless, circumstances under which such a glass surface may have a structure representative (or at least reminiscent) of its bulk structure?

The temptation exists to assume a hydrated, swollen layer on any oxide surface
in contact with an aqueous solution. However, it is very doubtful whether this conclusion may justifiably be based on the evidence obtained with glasses. Evidence related to a swollen layer on glass in the majority of cases refers to solids containing large amounts of alkali ions, which show a pronounced tendency to exchange against $H^+$ or $H_2O^+$ ions. Such an exchange seems to be necessary to loosen the network sufficiently by hydrolysis of Si-O-Si and similar bonds in order to make swelling possible. The one exception to this rule is vitreous silica, where diffusion of “water” into the solid over a distance of at least a few molecular diameters has been assumed to be the rate determining step in the attack by alkaline solutions (ref. 50). On the other hand, the reaction of vitreous silica with water at room temperature proceeds only slowly (see Section IV).

An interesting case in point is alkali-free calcium silicate glass, especially in view of the evidence obtained for formation of a calcium silicate-rich surface layer on Na$_2$O-CaO-SiO$_2$ glasses (see Fig. 13). For CaSiO$_3$, a difference in electrokinetic properties indeed has been reported between a glass and a crystal of the same composition (ref. 22). In 0.01 M NaOH solutions of different CaCl$_2$ concentrations, the IEP shifts toward higher [CaSiO$_3$] values when crystalline CaSiO$_3$ is replaced by vitreous CaSiO$_3$ (see Fig. 14). The same shift is observed when crystalline CaSiO$_3$ is disordered at its surface by intensive grinding. These phenomena have been interpreted as indications of calcium ions being taken up less

![Diagram](image)

Fig. 14. $\zeta$ potential vs. CaCl$_2$ concentration. CaSiO$_3$ in 0.01 M NaOH. a: vitreous; b: + crystalline, $\bigcirc$ crystalline after intensive grinding (ref. 22).
92

easily into a solid whose surface layer is disordered, when compared with a solid which contains sites adapted to calcium ions such as might be expected on a crystalline calcium silicate. Similar phenomena have been reported in electrolyte solutions in dimethylsulfoxide (ref. 109), and for other solids such as Ca$_2$MgSi$_2$O$_7$ (ref. 110). If the interpretation given to these experiments is right, the data would show that at least on some alkali-free calcium silicate glasses, when ion exchange of Ca$^{2+}$ against 2 H$^+$ is prevented by proper choice of concentrations, the surface layer retains some essential characteristics of the bulk glass structure. Therefore, the presence of a swollen surface layer is excluded in these cases.

Recent measurements on the adsorption and desorption behavior of crystalline $\beta$-CaSiO$_3$ and Ca$_6$Si$_6$(OH)$_2$O$_{17}$ (ref. 111) support the absence of a hydrated surface layer. If a hydrated surface layer is present, both solids are expected to exhibit identical interfaces with aqueous solutions, since the Ca/Si ratio is equal, and the structures are closely related (ref. 112). Nevertheless, differences are found (ref. 111).

Careful analyses show that in such cases Ca$^{2+}$ and OH$^-$ ions are removed from the solution on contact with the solids concerned in nearly stoichiometric ratio. In similar cases, a "surface precipitation" of the corresponding hydroxides had been assumed to occur (ref. 113) due to the electric field near the phase boundary. It has, however, been argued (ref. 114) that if this would be true the solubility product of Ca(OH)$_2$ should be markedly dependent on whether the conditions correspond to the point of zero charge of Ca(OH)$_2$ or not. This relationship determines the field strength near the Ca(OH)$_2$/electrolyte solution interface; such an effect has not yet been reported. Moreover, in some cases adduced as evidence for a "surface precipitation", the absolute value of the $\zeta$ potential does not decrease on sorption of cations and hydroxyl ions on the surfaces concerned. If the electric field would be responsible for surface precipitation, then surface precipitation should continue leading to a thick layer of the corresponding hydroxide on the surfaces. This effect, however, is not found. Therefore, the phenomena appear to be better described as mutually stimulated adsorption of cations and hydroxyl ions. On increasing, say the CaCl$_2$ concentration at constant NaOH concentration (i.e., going from left to right in Figs. 14a and 14b), first energetically favorable calcium sites are occupied (at A in Fig. 15). This adsorption makes OH$^-$ adsorption or SiOH dissociation nearby (at B) possible, and this in turn makes other calcium sites at C, which in themselves are energetically unfavorable, suitable for occupation.

VII. INFLUENCE OF PORES

When the glass surface bears traces of phase separation, the chemical durability of the resulting glass is determined by that of the least stable phase if this
forms a continuous pore structure. If, however, the less stable phase is present as separate droplets, then the most stable phase determines the durability (ref. 53,115) (see also the discussion of the influence of \( \text{Al}_2\text{O}_3 \) on the durability of sodium borosilicate glasses in Section IV).

If the less stable phase forms a continuous pore structure, it is natural to expect diffusion of dissolved material through the pores to be the rate determining step in the attack by water. Indeed, for phase-separated sodium borosilicate glass, the penetration depth of the water is proportional to the square root of the time, which allows the process to be described as a diffusion with one diffusion constant (ref. 116-118). Similar observations have been recorded for a glass 25.47 \( \text{Na}_2\text{O} \), 25.47 \( \text{Al}_2\text{O}_3 \), 30.55 \( \text{B}_2\text{O}_3 \), 18.50 \( \text{SiO}_2 \) (ref. 119). The \( \text{SiO}_2 \)-rich phase, remaining after dissolution of the other phase, retained some characteristics of the initial glass. When the latter had been anisotropic (e.g., exhibited double refraction), then the resulting porous glass showed double refraction as well (ref. 120).

At which compositions and in which temperature range is phase separation to be expected? This question cannot, in the context of the present paper, be answered in general. Only a few glasses will be treated here; Fig. 16 shows the limit of phase separation for two kinds of alkali silicate glasses. At temperatures lower than those corresponding to the curves drawn, phase separation occurs. Figure 17 shows a contour map in the ternary diagram \( \text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2 \). At temperatures lower than those indicated, again phase separation must be expected in sodium borosilicate glasses. This is the case most encountered in practice.

In the porous layer, pore sizes down to 3 nm may be realized (ref. 53,123) but this is strongly dependent on the conditions prevailing during glass manufacture.

VIII. SOME APPLICATIONS

Use of Porous Glass as a Membrane

Quite a large number of publications, including patents, have been devoted to the use of porous glass as a membrane. In this respect, glasses form an ideal
Fig. 16. Limits of phase separation for glasses Li$_2$O-SiO$_2$ and Na$_2$O-SiO$_2$ (ref. 121).

Fig. 17. Contour map, showing temperatures below which phase separation occurs in glasses Na$_2$O-B$_2$O$_3$-SiO$_2$, as a function of composition. Composition in mol % (ref. 122).
basic material for making pores "tailor-made" in regard to their size for particular applications. Semipermeable membranes can be made which can be used in liquid junctions of electric cells or for reverse osmosis (ref. 124-131). However, special problems such as those connected with the stability of the glass need to be resolved.

Porous sodium borosilicate glass, which has a composition of Na₂O. 4 B₂O₃. 95 SiO₂ after leaching, has been investigated regarding its cation exchange properties by Altug and Hair (ref. 132-134). Two types of sites were found, differing in dissociation constant (pKₐ = 5.1 and 7, respectively). The selectivity toward ion exchange was found to be a function of porosity and degree of hydration; a relatively porous membrane shows a low selectivity. By decreasing the porosity through sintering, the selectivity toward K⁺ can be specifically increased such as to make it comparable to that of a K-electrode. Similarly, Hersh and Teter (ref. 135) characterized the surface of a porous glass of composition 0.179 K₂O. 0.113 ZrO₂. 0.27 Al₂O₃. 3.13 B₂O₃. 96.3 SiO₂ by the potential of a KCl concentration cell, in which the glass concerned was placed at the junction of the two solutions. This potential could be interpreted through a Donnan-Planck model with two types of Brønsted acid sites whose concentration corresponded to the bulk concentrations of Al₂O₃ and B₂O₃, respectively.

Origin of Glass Electrode Potentials

Although this subject is much too extensive to be covered in its entirety in this review, it is so important as to necessitate an introduction to some of the arguments presented.

It is known (see, e.g., ref 42) that such a potential may arise from two sources: 1) ion exchange (causing the so-called "boundary potential"); 2) diffusion of ions in a membrane (as such, the hydrated surface layer of the glass is thought to act). Relevant equations have been derived, among others, by Isard (ref. 136):

a) For the boundary potential:

\[ \phi = \text{constant} + \frac{nRT}{F} \ln \left( \frac{a_i^{1/n}}{K_{ij}^{1/n}} a_j^{1/n} \right) \]

(5)

if the activity \( a_i \) of ionic species \( i \) in the glass is related to its concentration in the glass \( c_i \) by \( a_i = (c_i)^n \); \( a_i \) is the activity of this species in the solution surrounding the glass; the species \( i \) and \( j \) exchange according to:

\[ I^+ (\text{glass}) + J^+ (\text{solution}) \rightarrow J^+ (\text{glass}) + I^+ (\text{solution}) \]

with an equilibrium constant:

\[ K_{ij} = \frac{a_j}{a_i} \frac{a_j}{a_i} \]

(6)
b) For the diffusion potential:

$$\psi = -\frac{RT}{F} \int_{\text{surface}} \left( \frac{1 - u_j/u_i}{c_i + c_j u_j/u_i} \right) \frac{a}{a} \ln \frac{a_i}{c_i} \, dc_i,$$

(7)

where $u_i$ is the mobility of ionic species $i$ in the surface layer.

The difficulty in applying these equations is that there is a paucity of data available on the mobilities. It can be argued that in a hydrated surface layer two diffusion potentials exist (at the interfaces bulk glass/hydrated layer and hydrated layer/aqueous solution, respectively), which counteract each other. However, they will cancel in exceptional cases only. Neither the mobilities nor their ratio can reasonably be expected to be constant in the surface layer. Thus, Wikby (ref. 137) found at the inner side of the hydrated layer a region of high electrical resistance at the depth where the alkali ion concentration jumps from its surface layer value to its bulk glass value (see Fig. 9).

In the absence of sufficient data, any discussion on the relative importance of the two types of potential must remain undecided. Some typical indirect arguments are the following:

1. Eisenman (ref. 42) concluded, from measurements of the mobilities of the ions concerned in the surface layer, that in most glass electrodes both diffusion and phase boundary potentials contribute to the total potential; but that whenever the potential vs. pH curve shows a "Nernst" slope, the phase boundary potential is most important. However, his assumptions concerning constancy of the mobility ratio of various cations in the hydrated surface layer, and of constant differences in standard chemical potentials of these ions, are not warranted in the light of later investigations (ref. 136-138).

2. Tadros and Lyklema (ref. 139) observed that a Na⁺ responsive glass electrode has no preference for Na⁺ over other cations with regard to chemisorption under the conditions where the electrode behaves ideally. The "affinity" of the hydrated layer for Li⁺, Na⁺ and K⁺ was found to be equal; thus, the surface potential is equal for all ions. This finding means that differences in selectivity of a glass toward Li⁺, Na⁺ and K⁺ are caused by differences in mobility only. However, if on the basis of this model the total potentials are thought to be due primarily to diffusion potentials, the mobility ratio for Na⁺ and K⁺ in the hydrated layer should be much larger than that reported by Eisenman (see Section III). A possible explanation for this discrepancy may be that the glasses investigated by Tadros and Lyklema (17.1 Na₂O, 11.7 B₂O₃, 1.22 Al₂O₃, 1.19 GeO₂, 68.7 SiO₂ and a similar K glass) differ from that employed by Eisenman (27 Na₂O, 4 Al₂O₃, 69 SiO₂) in having a smaller amount of non-bridging oxygen ions, both because of the former's lower alkali oxide content, and because of its B₂O₃ content ("boric acid anomaly", see Section I). This difference
might cause diffusion of alkali ions through the hydrated layer of the Eisenman glass to be fast and not very specific, such as to make the situation near the hydrated layer/bulk glass boundary decisive for the potential. In the surface layer of the Tadros and Lyklema glasses, on the other hand, differences between diffusion rates of various ions can become pronounced and may influence the potential to a large extent.

3. Karlberg (ref. 140) investigated the influence of removal of the hydrated surface layer and found that the presence of the gel layer caused only small changes in the selectivity of an electrode, but retarded the potential response. However, no data on the glass compositions investigated by Karlberg were supplied, thus, no comparison with Eisenman's or Tadros and Lyklema's results is possible.

In view of the uncertainty of the interpretation, the amount of information about the glass/electrolyte solution interface, which can be obtained from electrode potential measurements, is at present rather limited. Especially the lack of systematical variation in glass composition used for the electrodes is to be regretted, the more so because potentials and their time and concentration dependencies can be measured relatively easily and accurately.

It is hoped that in the near future more information will become available to elucidate glass electrode potentials.

REFERENCES
23 As ref. 10, p. 229.
53 As ref. 50, p. 244-247.
55 H.J. Oel, as ref. 49, paper I.16.
60 S. Dobos, Acta Chim. (Budapest), 69(1)(1971)43-48; CA 75, 80627w.
64 S. Dobos, Acta Chim. (Budapest), 69(1)(1971)49-57; CA 75, 80624t.
76 E.P. Dain, G.V. Kataeva and I.D. Tykhonski, Steklo, No. 2(1969)36-40; CA 75, 24612a.
86 W. Vogel, as ref. 3, p. 100.
89 Yu.V. Ragozhin and D.V. Rodina, Steklo, 2(1967)72-73; CA 71, 24387y.
102 F.R. Bacon, Glass Ind., 49(1968)554.
111 A.J.G. van Diemen and H.N. Stein, to be published.
118 M. Shimbo, Yogyo Kyokai Shi, 80(923/7)(1972)273-283.
121 As ref. 50, p. 50.
122 As ref. 50, p. 52.
124 W. Haller, US 3.607.702, CA 75, 147206d.
130 C.I. Cohen, US 3.615.958; CA 76, 63868d.
131 C.I. Cohen, US 3.615.958; CA 76, 63868d.