

## Interdiffusion of hydrogen and alkali ions in glass surfaces

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## INTERDIFFUSION OF HYDROGEN AND ALKALI IONS IN GLASS SURFACES

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The Boksay–Doremus theory on the interdiffusion of hydrogen and alkali ions in glasses was extended by taking into account the association of hydrogen ions and non-bridging oxygen ions. In the derivation of the interdiffusion coefficient the bulk composition of the glass is taken into account. Theoretical concentration profiles were compared with experimental data, reported in literature, of alkali–alkaline earth–silicate glasses and of a sodium–aluminium–silicate glass. An essential feature of this extended B–D theory is, that the relative order of chemical durability of alkaline earth containing glasses is found by this theory without assuming excessive changes in individual diffusion coefficients.

### 1. Introduction

Doremus [1,2] extended the theory of Boksay et al. [3,4] on concentration profiles in the surface layer of alkali containing glasses which have been in contact with water, by introducing a concentration dependent interdiffusion coefficient of the form

$$\tilde{D} = D_A D_B / [c D_A + (1 - c) D_B] , \quad (1)$$

where  $D_A$  and  $D_B$  are individual diffusion coefficients of ions A and B, and  $c$  is the atom fraction of the alkali ion A originally present in the glass. Doremus compared calculated concentration profiles with experimental ones, reported in literature, and he showed that eq. (1) is superior to the assumption of a constant diffusion coefficient. Nevertheless, the use of (1) must be considered as a trial, because it strictly holds for free interdiffusing cations A and B, whereas the non-bridging oxygen ions in the silicate anion groups  $\equiv \text{SiO}^-$  (further denoted as  $\text{O}^-$ ) trap and thus localize most of the interdiffusing  $\text{H}^+$  ions. In this paper we extend the Boksay–Doremus theory by taking this association into account. The relevant interdiffusion coefficient can be derived following Helfferich [5]. Alkaline earth-ions, which do not participate in the ion-exchange process [3], increase the number of non-bridging oxygen ions, whereas alumina decreases this number. Thus, the glass

composition must be taken into account in this derivation. It will be seen that by the present theory differences in durability between glasses can be explained without assuming excessive changes of the individual diffusion coefficients.

## 2. Theory

According to Boksay et al. [3,4] the diffusion in the glass must be considered with respect to a moving outer surface. If  $x$  is the distance of a plane in the glass from its initial surface and  $a$  is the rate of dissolution of the surface, then  $y$ , the distance from the actual surface at time  $t$ , may be expressed as

$$y = x - at \tag{2}$$

where it is assumed that  $a$  is constant with time. The diffusion equation in  $y$  coordinates with a concentration-dependent interdiffusion coefficient  $\tilde{D}$  is [1]:

$$(\partial c_1 / \partial t)_y = (\partial / \partial y) \tilde{D} (\partial c_1 / \partial y)_t + a (\partial c_1 / \partial y)_t, \tag{3}$$

Where  $c_1$  is the concentration of the diffusing alkali ion. In the steady-state  $(\partial c_1 / \partial t)_y = 0$ , and integration of eq. (3) with  $dc_1 / dy \rightarrow 0$  and  $c_1 \rightarrow c_1^0$  when  $y \rightarrow \infty$  yields

$$\tilde{D} dc_1 / dy = a(c_1^0 - c_1). \tag{4}$$

### 2.1. Interdiffusion coefficient of silicate glasses containing alkaline earth ions

In a glass with bulk composition:  $p$  mol %  $(M^{1+})_2O$ ,  $q$  mol %  $M^{2+}O$  and  $r$  mol %  $SiO_2$ , the mean number of non-bridging oxygen atoms per silicon tetrahedron is given by  $X = 2[(p + q + 2r)/r] - 4$ . The total concentration  $C_{O^-}^0$  (mol/l) of the non-bridging oxygen ions is given by  $XC_s$ , where  $C_s$  (mol/l) is the bulk concentration of the silicate tetrahedra, which follows from the density and composition of the glass. For convenience we divide  $C_{O^-}^0$  in parts  $C_{O_1^-}^0$  and  $C_{O_2^-}^0$  equivalent to the bulk concentrations  $C_1^0$  and  $C_2^0$  of the  $M^+$  and  $M^{2+}$  cations, respectively

$$C_{O^-}^0 = C_{O_1^-}^0 + C_{O_2^-}^0 \tag{5}$$

with

$$C_{O_1^-}^0 = C_1^0 \quad \text{and} \quad C_{O_2^-}^0 = 2 C_2^0. \tag{5a}$$

We assume that  $H^+$  ions can associate with any of the non-bridging oxygen ions. Association of  $H^+$  ions with non-bridging oxygen ions, which have  $M^{2+}$  ions in their vicinity, yields groups, which as a whole carry a positive charge. This charge, however, is compensated elsewhere by a lack of  $Na^+$ , i.e. by the negative charge of a non-bridging oxygen ion, as required by the electroneutrality. In total, it remains true that  $C_{O_2^-}^0$  non-bridging ions are required for the neutralization of the non-moving divalent ions at any point  $y$ ; We write formally:

$$C_{O^-}^0 = C_{O^-} + C_{OH} + C_{O_2^-}^0 \tag{6}$$

where  $C_{OH}$  is the concentration of associated  $H^+$  ions. The association of  $H^+$  ions with the non-bridging oxygen ions is taken into account by use of the degree of dissociation

$$\alpha \equiv C_{H^+}/C_H \tag{7}$$

where  $C_H$  is used for the total concentration of hydrogen.

In the following,  $H^+$  ions, which are not associated with non-bridging oxygen ions, are indicated by "free". These ions, however, must be thought of as bound to free electron pairs on bridging oxygen atoms and also to water molecules when present as in gel layers. This binding is much less tight than that of  $H^+$  in silanol groups. Of course, alkali ions are also bound to negative oxygen ions, but this binding is less tight than that of  $H^+$  in silanol-groups as well. Therefore the interdiffusion can be described in terms of "free"  $H^+$  and alkali ions. The equilibrium  $\equiv SiOH \rightleftharpoons \equiv SiO^- + H^+$  is assumed to be instantaneous compared with the interdiffusion process.

The Nernst–Planck flux equations for  $M^+$  ions and for total hydrogen are [5]:

$$J_1 = -D_1 [\text{grad } C_1 + (C_1 F/RT) \text{ grad } \phi] \tag{8}$$

$$J_H = -D_H [\text{grad}(\alpha C_H) + (\alpha C_H F/RT) \text{ grad } \phi] \tag{9}$$

where  $J$  is the flux,  $D$  is the individual (tracer) diffusion coefficient,  $F$  is the Faraday constant,  $T$  is the absolute temperature,  $\phi$  is the electrical potential and the subscripts 1 and H refer to  $M^+$  and hydrogen ions.

It has been assumed that coupling effects other than by electrical fields are negligible and activity gradients have been neglected. Moreover, the appearance of the tracer diffusion coefficients in (8) and (9) amounts to assuming that the mobilities in a tracer diffusion experiment, in which there are no gradients in ionic concentration, are equal to those in an interdiffusion experiment, involving concentration and electrical potential gradients. Doremus [6] found that the interdiffusion of sodium and potassium ions in a sodium–lime glass at a temperature not too close to the transition temperature can be described by eq. (1) with constant  $D_A$  and  $D_B$ . The problem whether or not a mixed alkali effect would cause  $D_1$  and  $D_H$  to vary with ionic concentration has not yet been solved. Just like Doremus [1] we assume that for interdiffusion of hydrogen ions and alkali ions near room temperature  $D_1$  and  $D_H$  are independent of the changing ionic ratio in the glass.

Electroneutrality and absence of electric current requires that

$$\alpha C_H + C_1 + 2 C_2^0 = C_{O^-} + C_{O_2^0}$$

or with (5a)

$$\alpha C_H + C_1 = C_{O^-} \tag{10}$$

and

$$J_1 + J_H = 0 . \tag{11}$$

Combination of eqs. (8) to (11) to eliminate  $\alpha C_H$  and  $\text{grad } \phi$  gives

$$J_1 = - \{D_H D_1 / [D_H(C_{O^-} - C_1) + D_1 C_1]\} (C_{O^-} - \text{grad } C_1 - C_1 \text{ grad } C_{O^-}). \quad (12)$$

Since it is assumed that  $H^+$  ions can associate with any of the non-bridging oxygen ions, the mass action law with constant activity coefficients may be written as

$$(C_{O^-} + C_{O_2^-}) C_{H^+} / C_{OH} = K_{OH} = \text{constant}. \quad (13)$$

Strictly speaking, the dissociation constant of SiOH groups will be different for groups with a mobile alkali ion or with a much less mobile alkaline earth ion in their vicinity. However, for simplicity this difference is neglected. Thus, one dissociation constant  $K_{OH}$  is considered to describe the dissociation of  $\equiv \text{SiOH}$  groups.

With eqs. (6), (7) and (10), eq. (13) leads to a quadratic equation for  $C_{O^-}$  with the solution

$$C_{O^-} = \frac{1}{2}(C_1 - C_{O_2^-}^0 - K_{OH} + A) \quad (14)$$

where

$$A = [(C_1 - C_{O_2^-}^0 - K_{OH})^2 + 4(K_{OH} C_{O_2^-}^0 + C_{O_2^-}^0 C_1 - C_{O_2^-}^0 K_{OH})]^{1/2}. \quad (15)$$

Differentiation of eq. (13) yields

$$\text{grad } C_{O^-} = \frac{1}{2} [1 + (C_1 + C_{O_2^-}^0 - K_{OH})/A] \text{ grad } C_1. \quad (16)$$

Substituting  $C_{O^-}$  and  $\text{grad } C_{O^-}$  in eq. (12) by eq. (14) and (16) one obtains, after rearrangement, the flux equation:

$$J_1 = -\tilde{D} \text{ grad } C_1 \quad (17)$$

where

$$\begin{aligned} \tilde{D} = D_1 [A(A - K_{OH} - C_{O_2^-}^0) - C_1(C_1 + C_{O_2^-}^0 - K_{OH})] / [A(A - K_{OH} - C_{O_2^-}^0) \\ - C_1 A(1 - 2 D_1/D_H)]. \end{aligned} \quad (18)$$

Eq. (18) reduces to Helfferich's [5] eq. (19) if  $C_{O_2^-}^0$  is equalized to zero.

Substitution of  $\tilde{D}$  in eq. (4) yields, after some rearrangement, the differential equation

$$\begin{aligned} dC_1/dz = (C_1^0 - C_1) [A(A - K_{OH} - C_{O_2^-}^0) - C_1 A b] / [A(A - K_{OH} - C_{O_2^-}^0) \\ - C_1(C_1 + C_{O_2^-}^0 - K_{OH})] \end{aligned} \quad (19)$$

where  $b = 1 - 2D_1/D_H$  and  $z = ay/D_1$  are dimensionless parameters and  $A$  is given by eq. (15).

## 2.2. Interdiffusion coefficient of a sodium–aluminium silicate glass

In the present paper we compared calculated steady-state concentration profiles with the experimental concentration profiles of a leached sodium–aluminium silicate

glass reported by Boksay et al. [7]. The glass investigated by these authors has the composition 22 mol % Na<sub>2</sub>O; 5.5 mol % Al<sub>2</sub>O<sub>3</sub> and 72.5 mol % SiO<sub>2</sub>. Assuming a density  $2.5 \times 10^3 \text{ kg m}^{-3}$ , the concentrations of these oxides are 8.77; 2.19 and 28.88 mol l<sup>-1</sup>, respectively. The aluminium atoms were supposed by Boksay to form tetrahedra.

From the composition data it follows that the average number of non-bridging oxygen atoms per tetrahedron is 0.395. Thus, the concentration of non-bridging oxygen atoms is 13.14 mol l<sup>-1</sup>. Boksay et al. [7] assumed that all the aluminium atoms in the glass investigated form tetrahedra and that none of the oxygen atoms attached to an aluminium ion are non-bridging oxygen ions. If it is assumed that these assemblies of atoms do not tend to take up protons like the non-bridging oxygen ions in the silicate anion groups, then the presence of aluminium would account for the retention of 25% of the sodium ions in the glass phase during the treatment with water. However, since the experimental value is about 15%, Boksay et al. [7] assumed an interaction between tetrahedra and protons.

It should be noted that in the glass, investigated by Boksay, the occurrence of Al<sup>3+</sup> in six-fold coordination with three bridging oxygens, one non-bridging and two passive oxygens, which are bridging oxygens belonging to adjacent tetrahedra, is not excluded [8,9]. This octahedral structure may conceivably have properties different from the AlO<sub>4</sub>-group. If it is assumed that both sodium ions, required to preserve electrostatic neutrality of such an octahedral group, are exchangeable by protons, and, moreover, that the non-bridging oxygen atoms are distributed at random over the Si and Al ions, forming the octahedral structure with the latter ions, then a retention of 15% of the sodium ions results. The agreement between the calculated and experimental values of the retention can of course be fortuitous. We shall now leave aside the actual cause of the retention of the sodium ions.

The retention of the sodium ions is taken into account by introducing the total exchangeable sodium concentration in the bulk  $c_{\text{Na}}^0$

$$c_{\text{Na}}^0 = C_{\text{Na}}^0 - C_{\text{Na},r}^0 \tag{20}$$

where  $C_{\text{Na}}^0$  is the total concentration in the bulk and  $C_{\text{Na},r}^0$  is the experimental concentration of the retained sodium ions. In this special case  $C_{\text{Na},r}^0 = 2.65 \text{ mol l}^{-1}$  and  $C_{\text{Na}}^0 = 17.54 \text{ mol l}^{-1}$ .

In fact, at least three association constants for H<sup>+</sup> ions must be distinguished. However, just like in the previous sub-section, this difference is neglected and we introduce only one type of O<sup>-</sup> group with which H<sup>+</sup> ions associate. The relation which replaces eq. (6) is

$$C_{\text{O}^-}^0 = C_{\text{O}^-} + C_{\text{OH}} \tag{21}$$

where  $C_{\text{OH}}$  is again the concentration of associated H<sup>+</sup> ions and  $C_{\text{O}^-}^0$  is the total concentration of O<sup>-</sup> in the bulk and equals  $c_{\text{Na}}^0$  in magnitude ( $= 14.89 \text{ mol l}^{-1}$ ). On introducing  $c_{\text{Na}}$ , the interdiffusion coefficient, which can be derived in the same way as in the previous subsection, is equal to the original Helfferich interdiffusion

coefficient [5].  $\tilde{D}$  and  $A$  can be obtained from eqs. [18] and [15] by substitution of  $c_{\text{Na}}$  for  $C_1$  and by omitting the terms with  $C_{\text{O}_2}^0$ .

Numerical solutions of eq. (19) and its sodium–aluminium–silicate glass analogue were obtained with the boundary condition  $C_1$  and  $c_{\text{Na}} = 0$ , respectively, when  $y = 0$ , using the fourth-order Runge–Kutta method on a Hewlett Packard HP-97 calculator.

### 3. Comparison with experimental data and discussion

#### 3.1. Silicate glasses containing alkali earth ions

In table 1 experimental data, reported in the literature, are compiled.

Curves of concentration as a function of the dimensionless parameter  $z = ay/D_1$ , calculated with the  $C_{\text{O}_2}^0$ - and  $C_{\text{O}_2}^0/2$  values of the Li glass, are given in fig. 1 for various values of  $(D_1/D_{\text{H}})K_{\text{OH}}^{-1}$ . If  $K_{\text{OH}} < 0.1$  and  $0.05 < (D_1/D_{\text{H}})K_{\text{OH}}^{-1} < 500$  differences in  $K_{\text{OH}}$  do not noticeably influence the course of the curves.

We cannot fit the experimental curve (ref. [10], curve g, fig. 5) exactly to one of the theoretical curves. In fig. 1a a curve is shown which fits rather neatly to the lower part of the experimental curve, but the upper part is too steep. From  $z_{1/2}$ , i.e. the  $z$  value for which  $C = \frac{1}{2}C^0$ , of this curve and Baucke's [10]  $a$  and  $y_{1/2}$  values, we calculate  $D_{\text{Li}} = 2.4 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$ . In order to obtain the same  $D_{\text{Li}}$  value as calculated from the bulk resistivity,  $D_{\text{Li}} = 1.6 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$  [9,1],  $z_{1/2}$  must be equalized to  $3.2 \times 10^{-3}$ , corresponding to the theoretical curve with  $(D_1/D_{\text{H}})K_{\text{RH}}^{-1} \approx 500$ . Like Doremus [1], we attribute the discrepancy between experimental and theoretical curves to the small depth of the surface layer (30 nm) and the limited resolution of the technique ( $\approx 4$  nm), so that the lithium concentration profile appears to be more spread out than it actually is.

From fig. 1 it is apparent that the inflexion in the curves disappears when  $(D_{\text{K}}/D_{\text{H}})K_{\text{OH}}^{-1} < 0.2$ . Figure 2 shows the theoretical curves for Boksay's [3] potassium glass 4. The experimental curve can be fitted to the curve with  $(D_{\text{K}}/D_{\text{H}})K_{\text{OH}}^{-1} = 0.05$ . We have also plotted in fig. 2 the  $\tilde{D}/D_{\text{K}}$  values for this curve. From the  $z_{1/2}$ ,  $y_{1/2}$  and  $a$  values we calculate  $D_{\text{K}} = 3.6 \times 10^{-13} \text{ m}^2 \text{ h}^{-1}$ . The  $\tilde{D}/D_{\text{K}}$  values are nearly constant. This explains why Boksay [3] could fit the experimental data with a theoretical curve based on a constant diffusion coefficient. With  $\tilde{D}/D_{\text{K}} \approx 1.6$ , we find the same diffusion coefficient  $\tilde{D} = 5.8 \times 10^{-13} \text{ m}^2 \text{ h}^{-1}$  as calculated by Boksay.

So far our treatment is equivalent to the use of the interdiffusion coefficient eq. (1). However, with eq. (1), the different concentration profiles ( $y_{1/2}$  values) of the glasses which differ only in the percentages of the composing oxides, can only be explained by assuming different  $D_1/D_{\text{H}}$  values and/ or  $a$  values. From the experimental curves (ref. [11], figs. 1–4, we deduce approximately the same  $a$  values for the glasses S<sub>1</sub>–S<sub>4</sub>. Figure 3 shows the theoretical steady-state curves for Wikby's [11] glasses and fig. 4 shows those for Boksay's [3] glasses 2 and 3, all calculated

Table 1  
Compilation of experimental data and composition of glasses.

Ref.	Glass	Glass composition (mol %)	$C_{CO_2}^0$ (mol l <sup>-1</sup> ) a)	$\gamma^{1/2}$ ( $\mu\text{m}$ ) b)	Temp. °C	Hydration Time (h)	$a$ (nm h <sup>-1</sup> )
[10]	Li	25 Li <sub>2</sub> O	27	0.018	50	15	0.10
[11,12]	S <sub>1</sub>	22 Na <sub>2</sub> O 10 CaO	26.6	0.3	25	190	
	S <sub>2</sub>	22 Na <sub>2</sub> O 6 CaO	23.3	0.8	25	190	
	S <sub>3</sub>	21.4 Na <sub>2</sub> O 6.4 CaO	23.1	0.5	25	190	0.02 c)
	S <sub>4</sub>	22 Na <sub>2</sub> O 4 CaO	21.6	1.3	25	190	
[3]	B <sub>2</sub>	28 Na <sub>2</sub> O 4 SrO	25.7	50	40	144	
	B <sub>3</sub>	20 Na <sub>2</sub> O 12 SrO	24.4	8	40	288	
	B <sub>4</sub>	20 K <sub>2</sub> O 12 SrO	22.2	4	40	>240	88.7
	Dole	21.4 Na <sub>2</sub> O 6.4 CaO	23.1	0.8	20	312	
[13]				2.4	40	312	

a) Calculated with  $d = 2.3 \text{ g cm}^{-3}$  and  $q = 5$  for the Li glass and  $d = 2.5 \text{ g cm}^{-3}$  for the other glasses.

b) Distance at which  $C_1/C_1^0 = \frac{1}{2}$ , deduced from the experimental concentration profiles or equalized to the reported gel layer thickness [12].

c)  $V_1$  of ref. [14].



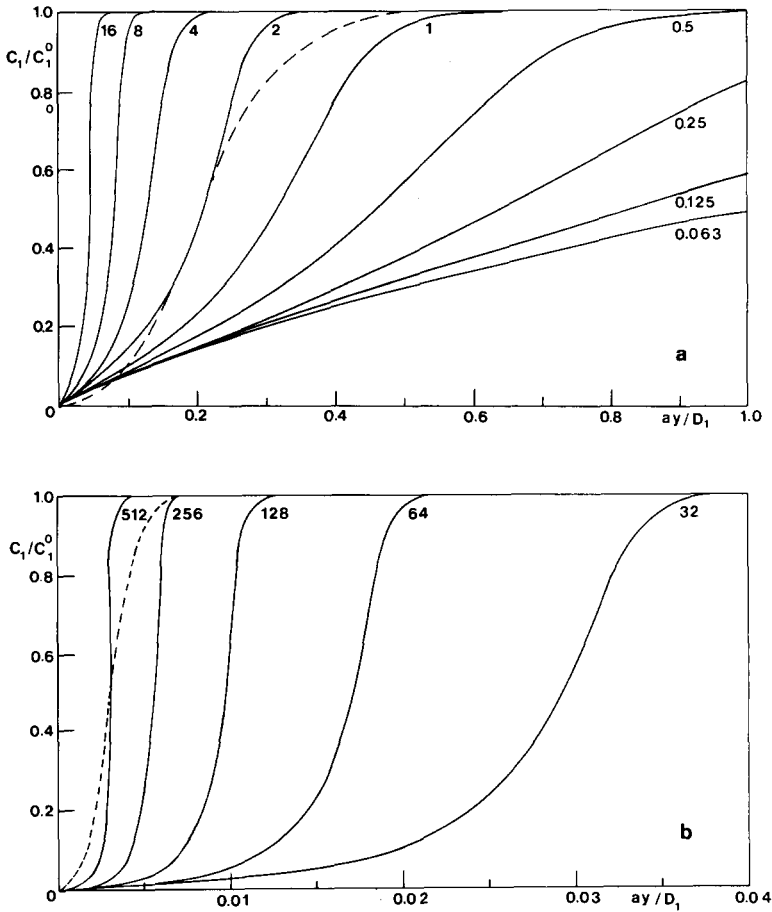


Fig. 1. a and b. Concentration profiles for the lithium silicate glass of table 1, calculated with different values of  $k = (D_1/D_H)K_{OH}^{-1}$  (on curves). The experimental curve (curve g, fig. 5 of ref. [10] is fitted with the point  $C_1/C_1^0 = 0.5$  to calculated curves with  $k = 2$  and 512 respectively.

with the same value of 50 for  $(D_{Na}/D_H)K_{OH}^{-1}$ . The sodium bulk concentrations of Wikby's glasses are all nearly the same, yet, the calculated curves have different  $z_{1/2}$  values. The relative position of the calculated curves is independent of the value of  $(D_{Na}/D_H)K_{OH}^{-1}$ .

The order of the  $z_{1/2}$  values,  $S_4 > S_2 > S_3 > S_1$  and  $B_2 > B_3$ , is the same as the order of the experimental gel layer thickness and  $y_{1/2}$  values. If it is assumed that  $D_{Na}$  is not very different for the four S glasses then it follows from the theoretical curves that in order to attain and to maintain the steady state, the outflow of alkali is such that  $S_1 < S_3 < S_2 < S_4$  or the chemical durability order is  $S_1 > S_3 > S_2 >$

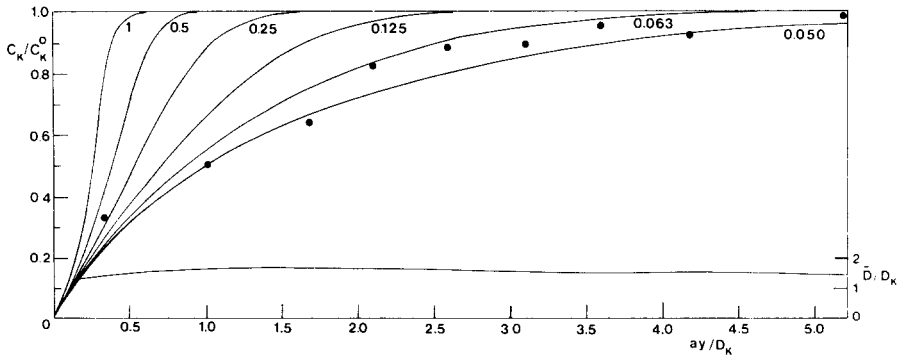


Fig. 2. Concentrating profiles for the potassium strontium silicate glass B<sub>4</sub> of table 1, calculated with different values of  $k = (D_K/D_H)K_{OH}^{-1}$  (on curves). The experimental curve [3] is fitted with the point  $C_K/C_K^0 = \frac{1}{2}$  to the calculated curve with  $k = 0.05$  for which the  $\bar{D}/D_K$  curve is also shown.

S<sub>4</sub>, as was also found experimentally [11]. The agreement is only qualitative. For a quantitative agreement some variations in  $(D_{Na}/D_H)K_{OH}^{-1}$  must be assumed. In fig. 4 it is shown that, if it is assumed that the  $a$  and  $D_{Na}$  values of the B<sub>2</sub> and B<sub>3</sub> glasses are the same, an increase of  $(D_{Na}/D_H)K_{OH}^{-1}$  of the B<sub>3</sub> glass with a factor 4 is sufficient to make the ratio of the  $z_{1/2}$  values of the B<sub>2</sub> and B<sub>3</sub> glasses more in agreement with the ratio of the experimental  $y_{1/2}$  values. However, for the B<sub>2</sub> and B<sub>3</sub> glasses the  $a$  values may also be different and in general variations in  $D_{Na}$  may occur too.

We shall now estimate  $D_H$  in the case of the Dole glass (S<sub>3</sub>), assuming that the diffusion coefficient  $D_{Na}$  in the transition layer is equal to that in the bulk. Taking for the resistivity  $\rho$  of the quenched samples a value about 10 times lower than for the annealed samples and using the Einstein equation  $D_{Na} = RT/\rho F^2 C_{Na}$ , we find  $D_{Na} = 6 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$  at 20°C. With  $y_{1/2} = 0.8 \text{ }\mu\text{m}$  and  $a$  about  $0.02 \text{ nm h}^{-1}$  the value 0.075 results for  $z_{1/2}$ . This value corresponds to a curve with  $(D_{Na}/D_H)K_{OH}^{-1} \approx 8$ . The value of  $D_H$  depends strongly on the value chosen for  $K_{OH}$ . According to Dugger et al. [15] the dissociation constant of surface silanol groups is  $10^{-6} - 10^{-8}$ . With  $K_{OH} = 10^{-7}$  the value  $D_H = 7.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$  follows.

However,  $D_H$  can be several orders higher or lower. From our radio-tracer experiments [16], in which concentration profiles in silica gel films were measured after different immersion times in alkaline  $^{24}\text{Na}^{82}\text{Br}$  solutions, we found with  $K_{OH} = 10^{-7}$   $D_H = 10^{-14} \text{ m}^2 \text{ s}^{-1}$  (and  $D_{Na} = 10^{-18} - 10^{-15} \text{ m}^2 \text{ s}^{-1}$ ).

This  $D_H$  value was also evaluated taking into account the association of  $\text{H}^+$  ions with non-bridging oxygen ions as in the present paper. We note that the  $D_H$  values, calculated in the present paper, are several orders in magnitude greater than the value  $D_H$  estimated by Doremus [1] from Baucke's [10] lithium silicate glass data.

Doremus,  $D_H$ , however, must be considered to be an apparent diffusion constant, referring to total hydrogen.

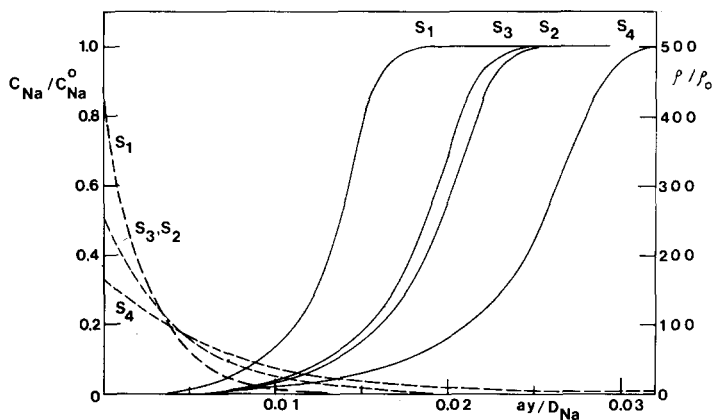


Fig. 3. Concentration profiles (—) and resistivity curve (-----) calculated for Wikby's [11,12] glasses  $S_1$ – $S_4$  of table 1 with  $k = (D_{Na}/D_H)K_{OH}^{-1} = 50$ .

If in eq. (9), in which  $J_H$  is the flux for total hydrogen and  $D_H$  stands for  $D_{H^{free}}$ ,  $\alpha$  is assumed to be constant so that  $grad(\alpha C_H) = \alpha grad C_H$ , then  $J_H$  can be written in terms of  $D_{app.} = \alpha D_{free}$ .

The constancy of  $\alpha$  holds in the case of self-diffusion in a traced chelating resin [17], but of course not in the present case. The above is merely to give an indication why our  $D_H$  values are much greater than  $D_H$  values of Doremus. Moreover, the values of  $D_{alkali}$  are found to be smaller than the  $D_H$  values at variance with Doremus. As  $D_H$  refers to the free  $H^+$  ions, this can be related to the smaller dimen-

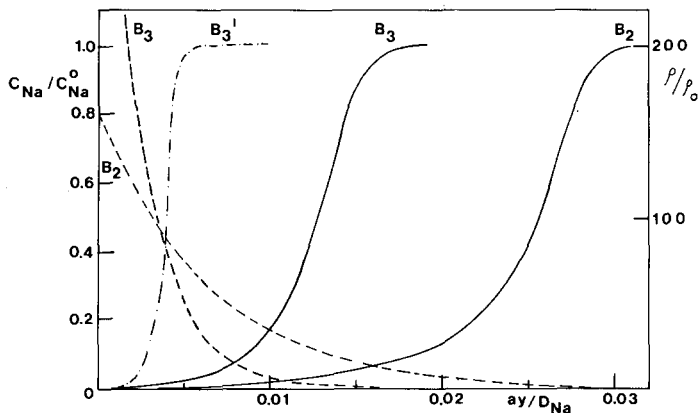


Fig. 4. Concentration profiles (—) and resistivity curve (-----) calculated for Boksay's [3] sodium glasses  $B_2$  and  $B_3$  of table 1 with  $k = (D_{Na}/D_H)K_{OH}^{-1} = 50$ . Curve  $B_3^1$  (- · - ·) has been calculated with  $k = 200$ .

sions of the protons compared with those of the alkali ions. Consequently, the free protons encounter less resistance in moving through the lattice. Of course, although  $D_{\text{alkali}} \ll D_{\text{H}}$ ,  $J_{\text{alkali}} + J_{\text{H}} = 0$  on account of the coupling with the electrical field set up to maintain electrical neutrality.

The theoretical curves differ in two important aspects from the experimental concentration profiles of the sodium glasses. The  $C_1/C_1^0$  values in the outer section of the experimental concentration profiles are higher and the slope lower compared with the theoretical curves (which were calculated with the condition  $C_1 = 0$  when  $z = 0$ ). The second difference refers to the resistivity curves. In fig. 3 and 4 we have plotted the resistivity curves, which were calculated using the Einstein equation and with the relation  $\rho^{-1} = \sum C_i \lambda_i / 1000$ , where  $\lambda_i$  is the equivalent conductivity of ion  $i$ . The use of these relations is compatible with the assumptions leading to eq. (18) which ignore the possibility of a mixed alkali effect. Assuming that  $D_1$  in the surface layer is equal to  $D_1^0$  in the bulk glass, the relation

$$\rho/\rho_0 = [C_1/C_1^0 + (C_{\text{H}^+}/C_1^0)/K_{\text{OH}}k]^{-1} \tag{26}$$

can be derived, where  $\rho_0$  is the bulk resistivity and  $k = (D_1/D_{\text{H}})K_{\text{OH}}^{-1}$ . The values of  $C_{\text{H}^+}$  follows from eqs. (7), (10) and (14). Calculations show that  $C_{\text{H}^+} + K_{\text{OH}}^{-1}$  is nearly independent of the value of  $K_{\text{OH}}$  used in the calculation of the concentration profiles for  $K_{\text{OH}} < 0.01$ .

According to the theoretical resistivity curves the resistivity increases sharply from the region where the alkali concentration rises rapidly to its bulk value, towards the solid/electrolyte interface. This increase of the resistivity increases with increasing durability of the glass. This is in agreement with the experimental facts [11]. However, Wikby [11] located the surface resistance in a small region only. Between the electrolyte/solid interface and the region of the surface resistance, the resistivity of the surface layer is according to Wikby et least a factor 5 lower than that of the bulk glass\*.

Both deviating aspects of the theoretical curves can be explained by Boksay's [3] assumption that a structural transformation starts when the alkali ion concentration in the layer has been diminished to a certain low value. This transformation is the breaking of silicon-oxygen bonds, which leads to a gel layer with a loosened structure. This gel layer formation is the cause of a fall-back of the resistivity curve after the initial rise and of the low concentration gradient of the outer region. According to Boksay and Lengyel [17] a certain proportion of alkali ions cannot diffuse out of the layer because of the existence of impasses in glasses, which remain intact to some extent when the network disintegrates.

\* We can obtain  $\rho/\rho_0$  curves with a maximum at the foot of the rising part of the  $C_1/C_1^0$  curves, when  $D_1$  and  $D_{\text{H}}$  of eq. (8) and eq. (9) are special functions of the changing ionic ratio in the glass, which simulate the mixed-alkali effect. The relative positions of the concentration profiles of the S and B glasses do not change and the maximum of the  $\rho/\rho_0$  curve increases with the durability. However, when the mobilities of the  $M^+$  ions at the surface are chosen not higher than in the bulk glass, the  $\rho/\rho_0$  curves increase again with diminishing  $C_1/C_1^0$ .

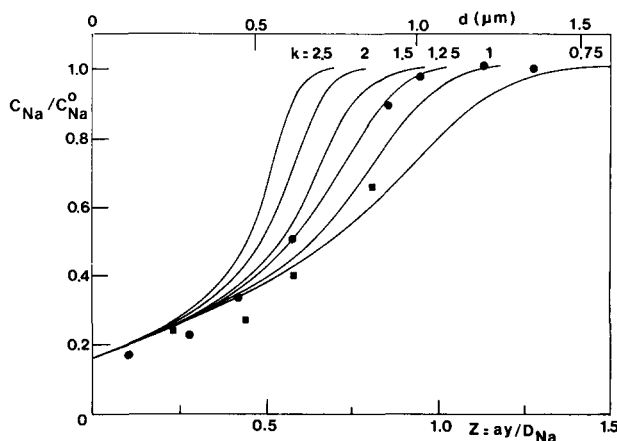


Fig. 5. Concentration profiles for Boksay's [7] sodium-aluminium silicate glass calculated with different values of  $k = (D_{Na}/D_H)K_{OH}^{-1}$  (on curves). The experimental results [7] of the specimen indicated by the full circles has been fitted to the curve with  $k = 1.25$ .

### 3.2. Sodium aluminium silicate glass

Figure 5 shows calculated sodium profiles with various  $k = (D_{Na}/D_H)K_{OH}^{-1}$  values for the sodium-aluminium glass discussed in sub-section 2.2. These curves were calculated with  $K_{OH} = 10^{-7}$ . However, curves with the same  $k$  but different  $K_{OH}$  are practically the same for  $K_{OH} < 0.01$ . This also holds for the  $C_{H^+}/K_{OH}$  curves. The curves with  $k = 1.25$  is a good fit to the experimental values of the specimen indicated by full circles. Since the value of  $a$  is not known  $D_{Na}$  cannot be calculated. If  $a$  is taken  $0.1 \text{ nm h}^{-1}$ ,  $D_{Na} = 3 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$  would result. The value of  $D_H$  depends on the value of  $K_{OH}$  and will be several orders of magnitude greater than  $D_{Na}$ .

In fig. 6  $D/D_{Na}$ ,  $C_{H^+}/K_{OH}$  and  $\rho/\rho^0$  have been plotted as a function of the distance parameter  $z$  for  $k = 1.25$ . The calculation of  $\rho/\rho^0$  was performed with eq. (26) neglecting the contributions of the retained sodium ions to  $\rho^{-1}$  and  $(\rho^0)^{-1}$ .

The calculated  $\rho/\rho^0$  curve shows a maximum and decreases to about 0.015 at the surface. This maximum is related to the sharp increase of  $C_{H^+}/K_{OH}$  towards the surface.

The  $\phi(z)$  curve, calculable from eqs. (8), (9) and (11) with use of the calculated values of  $C_{H^+}$  and  $c_{Na}$  and with the condition  $\phi = 0$  in the bulk of the solid, has the same shape as the  $\rho/\rho_0$  curve.

The function  $I(z) = \int_z^{\infty} (\rho/\rho_0 - 1) dz$  has a faint maximum near the surface, which is contrary to the experimental surplus resistance curve [7].

Further on, however, the  $I(z)$  curve is in agreement with the experimental curve. From the theoretical curves three experimental facts, apart from the sodium con-

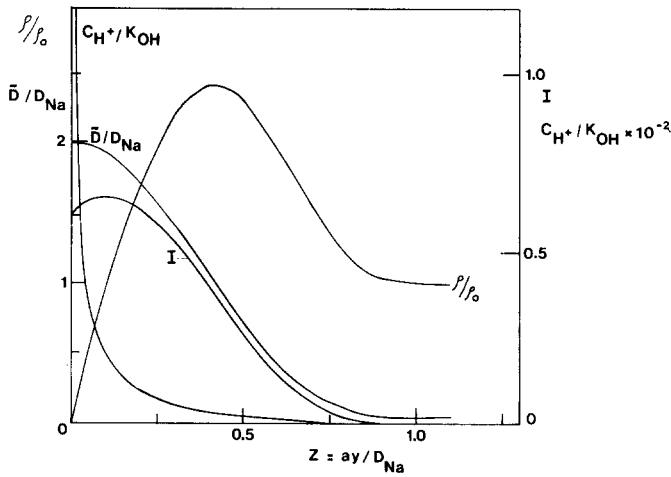


Fig. 6. Calculated resistivity ( $\rho/\rho_0$ ), surplus resistance ( $I$ ), interdiffusion coefficient ( $\bar{D}/D_{Na}$ ) and free hydrogen ion concentration ( $C_{H^+}/K_{OH}$ ) curves, calculated with  $k = 1.25$  for the glass of fig. 5.

centration profile, can be explained: (i). The surface conductance of the rod shaped specimens which considerably exceeds that of the bulk conductance, (ii) this surface conductance stems for  $H^+$  and not from sodium ions; (iii) there is a barrier layer in the surface layer. Boksay et al. [7] attributed the surface conductivity, which is constant up to 60% humidity in the measuring vessel, to a stratum behind the barrier layer, and the additional term at higher humidities to a layer exposed directly to the influence of the atmosphere. We can only agree with the explanation of the additional term.

Our treatment of the interdiffusion of hydrogen and alkali ions in glass surfaces is of course still only an approximation to the true situation. Stress introduced into the glass by the interdiffusion, violating the assumption of constant individual diffusion coefficients, and changes in activity coefficients have been neglected. It is to be hoped that our treatment has indeed revealed one of the other unknown influences on  $\bar{D}$  as Doremus wished examined [1].

### Acknowledgement

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