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Influence of surface potential on the kinetics of glass reactions with aqueous solutions

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The kinetics of leaching of alkali silicate glasses in aqueous solutions may be correlated experimentally with the rate of alkali ion transfer across the glass–water interface. However, present theories based upon free ion diffusion fail to provide quantitative or qualitative agreement with experiment. The model proposed incorporates an electrostatic interaction derived from the surface potential and associated space charge layer in the surface region of the glass, and thus involves field-enhanced diffusion. It gives both qualitative and reasonable quantitative agreement with experimental observations.

1. Introduction

When a silica-based glass is immersed in water at temperatures up to 100° C, the rate of alkali ion extraction and, generally speaking, of dissolution is proportional initially to the square root of time, t. Later, however, it becomes directly proportional to t [1–3]. The time at which the transition from the first rate dependency to the second occurs depends on temperature and the composition of the glass. For example, it can vary from less than a few minutes at 50° C for a reactive glass, such as 15 (mol%) K_2O–$85SiO_2$, to as much as several thousand min at 60° C for a more durable commercial-type glass such as $15Na_2O$–$10CaO$–$75SiO_2$.

Current interpretations of such corrosion behaviour [3–6] assume that the $\sqrt{t}$ dependence arises from a diffusion of alkali ions to the glass surface, from which they pass into the aqueous environment. Maintenance of charge neutrality was postulated by Douglas and Isard [7] to involve a counter-diffusion of hydrogen ions from the solution into the glass. Theoretical descriptions of this corrosion phenomenon have been principally directed towards correlation of measured *static* alkali ion concentration profiles with the diffusional form of Fick's laws. Recently, Doremus [8] has shown that, by using an "effective" counter-diffusion coefficient, a diffusion model gives good agreement with the static concentrations profiles.

However, the diffusion formalism is not in accord with the *kinetics* of the corrosion process; in particular, the experimentally observed linear time dependence. Observations of related phenomena also are inconsistent with a simple diffusional model. For example, high alkali ion velocities in the surface regions of hydrated glass yield "diffusivities" several orders of magnitude greater than those in the bulk glass [2, 3]. Thus, it must be emphasized that models which correctly predict the form of the concentration profile are necessary but not sufficient to describe the kinetics of profile development.

The purpose of this paper is to demonstrate that the kinetics of glass corrosion can be quantified and qualified within the more general Fickean formalism upon realizing that alkali (modifier) ions do *not* move in a purely diffusional mode in the near-surface regions of the solid. This is because the negative surface potential generated when glass is immersed in water produces an electrostatic potential gradient in the surface region of the glass which greatly modifies the kinetics of alkali ion migration, and hence the dissolution rate. It will be shown that the inclusion of this electrostatic surface potential term into the diffusion equation helps bring theory and observation into closer accord.

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2. Analytical approach

2.1. Origin of the surface potential

In general, the electrostatic potential at the interface between two material phases differs from that of the bulk potential of either phase. This potential arises in several ways, for example, at silver-halide–aqueous interfaces [9] the chemical potential difference of Ag^+ ions in these phases provides a driving force for transfer of this ionic species from solid to solution. Since, in equilibrium, the electrochemical potential for each ion species must be equal across the phase boundary, a potential difference must exist between phases.

In the present case, the surface potential results from ion transfer between the aqueous phase and the glass surface [10]. In alkali silicate glasses, as in most siliceous materials in alkaline, neutral and moderately acidic environments, the surface is negatively charged [10, 11] due to strongly chemisorbed, nucleophilic hydroxyl groups. The corrosion process in alkali-based glasses has been observed to have no apparent effect on the surface potential [11].

2.2. Distribution of the surface potential

Previous analyses of glass dissolution kinetics have either ignored the existence of the negative surface potential, or tacitly assumed the potential to be localized in the aqueous phase, distributed between a compact layer of ions adsorbed on the surface and a diffuse space charge layer (Gouy layer) in the liquid. However, as Grimley [12] has pointed out, the solid must be treated on an equal basis with the liquid in determining the distribution of the potential across the interface, i.e., the potential distribution in each phase is determined by the free charge densities and relative dielectric constants of each phase. It can be shown on the basis of the relative dielectric constants of water (~ 78) and glass (~ 4), and the relative alkali ion densities (typically 10^{20-22} cm^{-3} for silica glasses with alkali activation energies $\leqslant 1$ eV), that the predominant potential drop will be in the space charge region of the glass, this extending to a depth (the Debye screening distance, λ) determined by the charge carrier density in the solid. Typically, values for λ of several microns are calculated [13]. Experimental evidence consistent with the existence of such space charge layers in silica-based glasses has been discussed by Holland [14].

It should be noted that invoking the surface potential and space charge layer in our model does not alter the validity of the hydrogen–alkali ion counter-diffusion charge neutralization model of Douglas and Isard. As was recently pointed out by Horn and Onoda [11], (this) "... ion exchange does not involve a net charge transfer and can occur through an electric double layer without added electric work ..."

Accordingly, the following analysis will explicitly include the influence of the distribution of potential in the near-surface regions of the solid on the kinetics of alkali ion migration, which in turn determine the rate of glass dissolution.

2.3. Present model: assuming free diffusion

Following immersion of an alkali-silica glass in water, the alkali ion concentration in solution at time t, $Q(t)$, can be derived from Fick's equations. For free diffusion, where the driving forces are derived solely from the concentration gradient, $\partial N/\partial x$, these can be written

$$J(x,t) = -D\frac{\partial N(x,t)}{\partial x} \qquad (1)$$

and

$$\frac{\partial N(x,t)}{\partial t} = D\frac{\partial N^2(x,t)}{\partial x^2} \qquad (2)$$

where D is the diffusion coefficient, and N is the mobile charge carrier concentration at (x, t). Equation 1 describes the alkali ion flux and Equation 2 the rate of accumulation of this diffusing species at (x, t). The assumptions made in this analysis are that the solid is isotropic, of infinite dimensions normal to the x direction and semi-infinite in the direction x, and that D is a constant. We choose for simplicity the origin, $x = 0$, at the solid–solution interface, an initially uniform free alkali ion concentration in the solid of N_0, and an initial zero concentration of alkali in solution. Defining the starting conditions then as $N(0, t) = N_0$, $N(x, 0) = 0$, $(x > 0)$, the general solution for Equation 2 is:

$$N(x,t) = N_0\left[1 = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad (3)$$

where the function erf (x) is defined as $(2/\sqrt{\pi})\int_0^x \exp(-\xi^2)\mathrm{d}\xi$, ξ being a dummy variable introduced to simplify integration.

The corresponding particle flux across the solid–solution boundary is given by Equation 1, namely,

$$J(x,t)|_{x=0} = -D\frac{\partial N(x,t)}{\partial x}\bigg|_{x=0}$$

$$= \frac{DN_0}{\sqrt{\pi Dt}}\exp\left(\frac{-x_2}{4DT}\right)\bigg|_{x=0}$$

$$= N_0\sqrt{\frac{D}{\pi t}} \qquad (4)$$

Thus, the total alkali concentration in solution at time t, $Q(t)$ is simply

$$Q(t) = \int_0^t J(0,\xi)\mathrm{d}\xi = 2N_0\sqrt{\frac{Dt}{\pi}} \qquad (5)$$

Hence, the expectation in glass–water leaching experiments, based on the tenets of present free diffusion theories, is that a parabolic law, $Q(t) \propto \sqrt{t}$, should be observed. As discussed above, however, this behaviour is observed in binary glasses only at short times.

3. Proposed model: surface field enhanced diffusion

Inclusion of an electrostatic surface gradient term modifies Equations 1 and 2 as follows

$$J(x,t) = -D\frac{\partial N(x,t)}{\partial x} + vN(x,t) \qquad (6)$$

and

$$\frac{\partial N(x,t)}{\partial t} = D\frac{\partial^2 N(x,t)}{\partial x^2} - v\frac{\partial N(x,t)}{\partial x} \qquad (7)$$

where v $(= \mu E)$ is the alkali ion velocity and μ its mobility. E is the electrostatic field $(= -\Delta\phi(x))$, ϕ being the potential which satisfies Poisson's equation:

$$\Delta^2\phi(x) = \frac{-e\Delta N(x)}{\epsilon} \qquad (8)$$

where $\Delta N(x)$ is the local non-equilibrium charge distribution, e the electronic charge, and ϵ the permittivity. Applying the same initial and boundary conditions as above, and assuming a constant surface electric field (hence constant v), the following solution modified with respect to that given in Equation 3 is obtained:

$$N(x,t) = \frac{N_0}{2}\left\{\left(1 - \mathrm{erf}\left(\frac{x-vt}{2\sqrt{Dt}}\right)\right)\right.$$

$$\left. + \exp\left(\frac{vx}{D}\right)\left(1 - \mathrm{erf}\left(\frac{x-vt}{2\sqrt{Dt}}\right)\right)\right\} \qquad (9)$$

The corresponding ion flux through the boundary can, by substitution of Equation 9 into Equation 6, be shown to be

$$J(0,t) = \frac{N_0}{2}\left\{2\sqrt{\frac{D}{\pi t}}\exp\left(\frac{-v^2 t}{4D}\right)\right.$$

$$\left. + v\left(1 + \mathrm{erf}\left(\frac{v}{2}\sqrt{\frac{t}{D}}\right)\right)\right\} \qquad (10)$$

Then, the total ion concentration in solution is given by

$$Q(t) = \int_0^t J(0,\xi)\mathrm{d}\xi$$

$$= \frac{N_0}{2}\left\{\int_0^t 2\sqrt{\frac{D}{\pi\xi}}\exp\frac{-v^2 t}{4D}\,\mathrm{d}\xi\right.$$

$$\left. + vt + v\int_0^t \mathrm{erf}\left(\frac{v}{2}\sqrt{\frac{\xi}{D}}\right)\mathrm{d}\xi\right\}$$

which can be simplified to yield

$$Q(t) = \frac{2N_0 D}{v}\left[\mathrm{erf}\left(\frac{v}{2}\sqrt{\frac{t}{D}}\right)\left(\frac{v^2 t}{4D} + \frac{1}{2}\right)\right.$$

$$\left. + \frac{v^2 t}{4D} + \frac{v}{2}\sqrt{\frac{t}{\pi D}}\exp -\frac{v^2 t}{4D}\right] \qquad (11)$$

This equation is central to our model, and should be contrasted with Equation 5, obtained for free diffusion.

4. Comparison of theory with experiment

Qualitatively, it can be seen that the limiting forms of Equation 11 for forced diffusion are

$$\lim_{t \to 0} Q(t) \propto \sqrt{t}$$

and

$$\lim_{t \to \infty} Q(t) \propto t$$

which are consistent with the experimental observations of Rana and Douglas [1, 2] and Douglas and El-Shamy [4]. These limiting forms can be clearly seen in Fig. 1, where $\log Q(t)$ versus $\log t$ (Equation 11) is plotted for a fixed v^2/D value.

Quantitative comparison with experiment presents greater problems, due in part to the difficulty of obtaining accurate data for leaching experiments (particularly at short times), but more

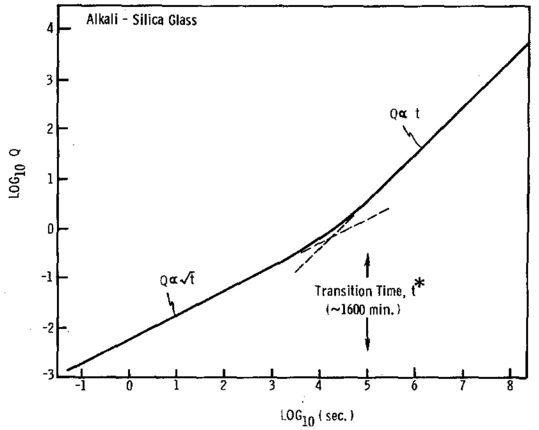

Figure 1 Theoretical relationship between total alkali ion concentration in solution, Q, and time of immersion, t, for an alkali-silica glass for which $v^2/D = 6.7 \times 10^{-4}$ sec^{-1}.

critically because of incomplete specification of experimental conditions – particularly with regard to electrostatic potentials at the glass–water interface. However, some meaningful tests of Equation 11 can be made by comparison of the experimental and predicted time at which the $\sqrt{t} \rightarrow t$ transition occurs. The procedure followed was to fit the experimental data to Equation 11 by varying the parameter v^2/D until the time at which the $\sqrt{t} \rightarrow t$ transition occurred corresponded with that observed experimentally. Given the diffusion coefficient D for the glass, it was then possible to calculate v, and hence the effective electrostatic field in the space charge region, E. Assuming the Einstein relationship between D and ion mobility μ to be valid, the value of E calculated was then compared to that anticipated on the basis of estimates of the surface potential ϕ_0, inferred from electrokinetic data [10], and of probable values for λ. The latter is determined by the mobile and fixed charge density in the solid, ΔN. In general, λ is $\propto (\Delta N)^{-1/2}$, and for the simple binary glasses treated here, ΔN is proportional to the alkali concentration in the glass. Thus, to a first approximation, the value of E generated by the above curve fitting procedure should be $\simeq \phi_0/\lambda$.

The experimental data used to test Equation 11 in the above manner was that published by Rana and Douglas [1, 2] for the binary glass $S_1(85SiO_2$–$15Na_3O)$. From Fig. 13a in Ref. [1], it is estimated that the linear segment commences at approximately 1600 min at 59.3° C. This point is then defined as the "transition time", t^*, since it is most easily determined for the experimental curves and the theoretical curves (Equation 11) – the latter by differentiating $Q(t)$ and determining the time at which dQ/dt is $\simeq$ constant (in the present analysis, constant to six significant figures as a basis for comparison). Although the choice is somewhat arbitrary, Rana and Dougal defined t^* as the mid-point between the $\sqrt{t} \rightarrow t$ segments in the experimental data. Fitting Equation 11 to the data in their Fig. 13a yields a value for v^2/D of 6.7×10^{-4} sec^{-1}.

4.1. Diffusion coefficient

Rana and Douglas [2] determined the diffusion coefficient for sodium ions in the S_1 glass at 60° C to be $D = 2.388 \times 10^{-14}$ cm^2 sec^{-1} from electrical conductivity experiments, and $D = 1.528 \times 10^{-12}$ cm^2 sec^{-1} from leaching experiments. Such discrepancies are typical, as mentioned earlier, and cast doubt upon the validity of a free diffusion model for the glass–water interface. Care must be taken in experimental measurements to ensure that the data fitted to the free diffusion model are taken at sufficiently short times to prevent the electrostatic component from generating significant errors. This point may be appreciated from consideration of Fig. 2, in which is plotted the ratio of the apparent diffusion coefficient D_A, to the true diffusion coefficient, D_T, as a function of the ratio t/t^* for S_1 glass, for which t^* is 1600 min. The apparent diffusion coefficient, D_A,

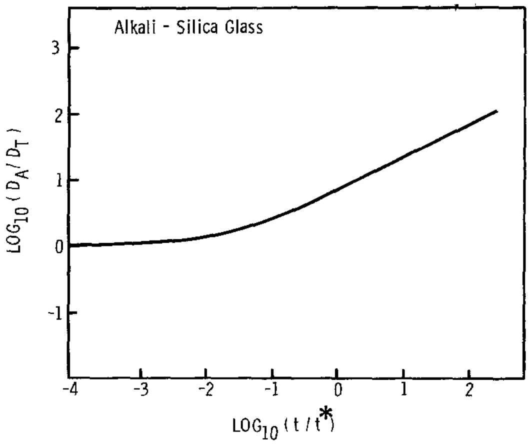

Figure 2 Relationship between the ratio (apparent diffusion coefficient, D_A, divided by true diffusion coefficient, D_T) and (immersion time, t, divided by "transition time", t^*), for an alkali-silica glass for which $v^2/D = 6.7 \times 10^{-4}$ sec^{-1}. The curve provides an indication of the relative error in determining the diffusion coefficient from leaching experiments as a function of sampling time.

is that which would be calculated by "forcing" the experimental data to a pure diffusion model.

Fig. 2 was generated by assuming $D_\mathrm{T} = 2.4 \times 10^{-14}\,\mathrm{cm^2\,sec^{-1}}$, i.e., the value from conductivity measurements and $v^2/D = 6.7 \times 10^{-4}\,\mathrm{sec^{-1}}$, characteristic of the S_1 glass. Substituting these values into Equation 11 yields ion concentrations for Q for each sampling time, t_0. Forcing the fit of Equation 11 to a free diffusion model defines D_A:

$$Q_{11}(t_0, D_\mathrm{T}) \equiv \frac{2N_0}{\sqrt{\pi}} \cdot \sqrt{D_\mathrm{A} t_0}$$

Equation 5 gives for a true diffusion situation

$$Q_5(t_0) = \frac{2N_0}{\sqrt{\pi}} \cdot \sqrt{D_\mathrm{T} t_0}$$

Subscripts 11 and 5 correspond to Equation 11 and 5, respectively. Then clearly $D_\mathrm{A}/D_\mathrm{T} = (Q_{11}/Q_5)^2$ for each time t_0. From the data, Fig. 2, it appears that errors begin to accumulate after ~ 16 min for a glass of $t^* \sim 1600$ min. Similar errors will appear when calculating activation energies for leaching from a pure diffusion model (Equation 5). Equation 11, on the other hand, contains the essential relationships to obtain the correct activation energies.

The effective electric field, E, has been calculated in Table I for both values of D obtained by Rana and Douglas. Values for λ were derived by assuming a surface potential of $\phi_0 = 200$ mV, the latter estimated from electrokinetic (ζ-potential) experiments on several glass compositions [10]. While no definitive relationship exists between ζ-potential and ϕ_0 at present, these quantities are generally regarded as being monotonically related, with ϕ_0 being $> \zeta$.

The calculated space charge electric fields and screening lengths shown in Table I appear realistic. Charles [13] for example, calculated a value for λ of 1.2 μm for a glass with an alkali ion density of $10^{21}\,\mathrm{cm^{-3}}$ with a defect energy of 1 eV. Surface potentials and screening lengths on the order of those calculated above are commonly observed at aqueous electrolyte–solid surfaces [15].

TABLE I Electrostatic parameters calculated for S_1 Glass ($15\mathrm{Na}–85\mathrm{SiO_2}$)

Diffusion coefficient ($\mathrm{cm^2\,sec^{-1}}$)	Effective electric field E (volts $\mathrm{cm^{-1}}$)	Debye length λ (μm)
$D \simeq 2.4 \times 10^{-14}$ (conductivity)	4×10^3	0.5
$D \simeq 1.5 \times 10^{-12}$ (leaching)	5.5×10^2	3.6

It is next of interest to consider the effect of alkali ion concentration on t^*. For simplicity consider a simple binary system, for which $D = 2.4 \times 10^{-14}\,\mathrm{cm^2\,sec^{-1}}$ (as above), $\phi_0 = 200$ mV, defect energy = 1 eV, and dielectric constant = 4.0. Charles [13] shows that an alkali ion concentration in a glass with the latter two properties exhibits a λ of $\simeq 1.2\,\mu$m. From these data and Table I, the approximate transition times presented in Table II can be generated.

Table II serves to illustrate the range of alkali ion leaching behaviour which may be encountered through the range of reactive to durable commercial glasses. Changes in composition or structure that affect alkali ion diffusion coefficients, mobility or defect activation energies, will also affect transition times.

Insight also can be gained concerning the temperature dependency of alkali ion leaching. Although this issue will not be discussed in detail here, inferences can be drawn by comparing Equation 11 and the data of Rana and Douglas. Qualitatively, Equation 22 predicts that the $\sqrt{t} \rightarrow t$ transition should occur earlier at elevated temperatures. Quantitatively, if the Einstein relationship between μ and D is valid, the ratio of t^*'s for a particular glass at temperatures T_1 and T_2 is given by

$$\frac{t^*(T_1)}{t^*(T_2)} \equiv \frac{D(T_1)}{D(T_2)} \frac{v(T_2)}{v(T_1)}^2 \simeq \frac{D(T_2)}{D(T_1)} \qquad (12)$$

Rana and Douglas provide data to check this relationship for $T_1 = 83.8°\,\mathrm{C}$, $D_\mathrm{T}(T_1) = 4.48 \times 10^{-15}\,\mathrm{cm^2\,sec^{-1}}$; and for $T_2 = 70.5°\,\mathrm{C}$, $D_\mathrm{T}(T_2) = 1.68 \times 10^{-15}\,\mathrm{cm^2\,sec^{-1}}$. From Fig. 16a in Rana and Douglas [1], $t^*(83.8)/t^*(70.5) = 1200$ min/3000 min = 0.4; while $D_\mathrm{T}(70.5°\,\mathrm{C})/D_\mathrm{T}(83.8°\,\mathrm{C}) = 0.37$ – a satisfactory agreement.

5. Concluding remarks

The rate of alkali ion transport through the surface layer of a glass has long been recognized as a critical parameter in glass dissolution, as well as in related phenomena such as static fatigue. Thus, it is important that all ion interactions in the surface regions be accounted for. We suggest that the free diffusion model, adopted hitherto, is deficient intrinsically, because it ignores the potential

TABLE II Dependence of transition time on alkali ion concentration, $N (D = 2.4 \times 10^{-14}$ cm^2 sec$^{-1})$

N_0	N (cm^3)	λ (μm)	E (volts cm^{-1})	t^* (sec)
"Reactive"	10^{22}	0.38	5.3×10^3	6.6×10^4 (~18 h)
	10^{21}	1.2	1.7×10^3	6×10^5 (~1 week)
	10^{20}	3.8	5.3×10^2	6.6×10^6 (~16 weeks)
	10^{19}	12	1.7×10^2	6×10^7 (~2 years)
	10^{18}	38	5.3×10^1	6.6×10^8 (~21 years)
"Quartz-like"	10^{17}	120	1.7×10^1	6×10^9 (~190 years)

gradient in the glass surface. Attempts to obtain agreement with experiment by applying second order corrections to the free diffusion model, for example, by invoking concentration-dependent diffusion coefficients or time-invariant concentrations, have not yielded analytical forms in either qualitative or quantitative agreement with experimental observations. Indeed, as Frischat [17] has commented recently "... the kinetic data obtained from leaching of glasses are still more or less inconsistent from a theoretical point of view ...".

Against this background, it has now been shown that insertion of an electrostatic term into Fick's equations give, in first order, the correct qualitative and reasonable quantitative agreement with experimental results. And, we would submit, there is sufficient independent evidence now available for the existence of surface fields in non-metallic solids to provide a solid basis for the inclusion of the effects of such fields in any analysis of surface-sensitive physical behaviour.

The "model" proposed also infers that extrinsic physical parameters which affect the space charge field also will affect leaching kinetics, e.g., sample treatment, solution pH and temperature, concentration of impurities or alloying elements in the glass, the presence of surface active adsorbates, etc.

In conclusion, the model proposed, involving surface field enhanced diffusion, is considered more realistic than the presently adopted free diffusion model as a basis for explaining the alkali leaching behaviour of glasses, and should help resolve some of the apparent anomalies reported in the literature. The analysis has also yielded a relationship between the total alkali concentration in solution and time of immersion (Equation 11) which is readily amenable to experimental test.

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