Finite-Difference Numerical Analysis of Phase-Boundary Reaction Models for Cesium Penetration into Glass

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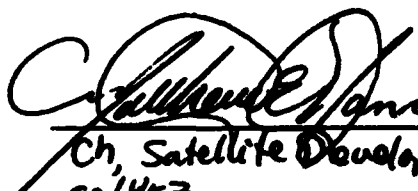El Segundo, CA 90245
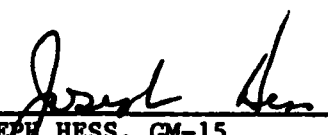
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Experimental data for the phase-boundary reaction and subsequent diffusion occurring when glass surfaces are exposed to aqueous cesium (Cs) have been theoretically analyzed. Partial differential equations resulting from a surface reaction followed by three possible modes of penetration, (a) simple diffusion, (b) interdiffusion, and (c) double diffusion of Cs, were numerically solved by means of a finite-difference technique. A model in

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which aqueous Cs^{+} is assumed to react rapidly with a time-dependent number of glass surface sites, followed by double-diffusion penetration, produced the best agreement with experiment. Cs diffusion coefficients of 2×10^{-16} and 3×10^{-17} cm^2/s were obtained. The value of the finite-difference solution technique is also discussed.

CONTENTS

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FIGURES

TABLE

I. INTRODUCTION

Reactions between glass and an aqueous solution are important in a number of technical areas. This is particularly true for the proposed encapsulation of radioactive wastes in vitreous media.[1,2] In this case the possible leaching by water of radioactive materials from the encapsulation matrix is of prime concern.[3] The liquid-glass interaction is comprised of a number of complicated processes; the importance of each depends on glass composition, reaction conditions, and the period of reaction.[4] Studying these processes during the early periods of glass exposure to solution results in some simplification. The "short time limit" investigation reduces the effects of surface etching yet still provides valuable information concerning the chemical processes occurring near the glass surface.[5]

Franek et al.[6,7] have investigated, both experimentally and theoretically, during the short time regime, the reactions between silicate glass surfaces and aqueous cesium chloride (CsCl) solutions. One interesting process observed was termed à "phase-boundary reaction." In this process an aqueous species, Cs^+, is believed to undergo a surface reaction prior to its diffusion into the glass. Their experimental data, presented as penetration profiles of Cs_2O into the glass as a function of the glass's solution-exposure time, were analyzed in terms of a quasi-empirical formulation. This model considered only a single species, Cs^+, which was allowed to diffuse into the glass subject to a time-varying surface-concentration boundary condition.[7] The surface-concentration boundary condition was taken empirically from the experimental data. This procedure results in a closed-form expression for Cs concentration as a function of penetration depth, exposure time, and Cs diffusion coefficient.

While fairly good agreement between the experimental data and calculated profiles is obtained, yielding a diffusion coefficient of 5×10^{-17} cm^2/s, the analysis is unsatisfying for several reasons. In order to extract the maximum chemical and mechanistic information from the data, it is desirable to model the entire reaction-diffusion process without empirically introducing

information. The reaction of aqueous Cs^+ with glass surface sites to yield
additional Cs species that diffuse into the glass is inherently a multi-
component process. Nonempirical modeling is then virtually impossible within
the framework of a single-component model. Also, parameters extracted from
the modeling, e.g. the diffusion coefficient, are model-dependent. It would
be highly desirable to compare penetration profiles predicted by different
physically meaningful reaction-diffusion models to study the effects on the
extracted parameters.

In this report, the phase-boundary reaction data of Franek et al.[7] are
reanalyzed in terms of two different mechanistic processes. Detailed descrip-
tions will be subsequently presented. Briefly, as outlined in Table 1, the
first process examined is the reaction of aqueous Cs^+ with a fixed number of
sites on the glass surface, yielding a Cs species that diffuses into the
glass. The second process examined is the rapid reaction of aqueous Cs^+ with
a time-dependent number of surface sites, followed by Cs diffusion into the
glass. While the times considered are brief enough to preclude significant
surface removal, they are sufficient for the etching process to generate a
time-dependent number of reaction sites. In addition to modeling the pene-
tration of Cs into the glass by simple diffusion, two other penetration models
were considered in this second process: first, Cs penetration as described by
the Doremus interdiffusion model,[8] and second, a two-pathway diffusion mechan-
ism. The interdiffusion and double-diffusion penetration models were not
developed for the first process. The reasons for this are given in the text.

All of these models yield partial differential equations (PDEs) that are
solved by means of standard finite-difference techniques. The principal
advantage of this approach is that it allows a consistent study of different
physically plausible processes. By studying the model solutions, one gains
information about which mechanisms actually occur within the glass. This
paper also demonstrates the value of formulating mechanistic models in terms
of PDEs and then directly solving these equations. This technique, which
provides a means of treating general multicomponent reaction-diffusion
processes, appears not to have previously received the attention its utility
warrants.

4

Table 1. Phase-Boundary Reaction Processes

Process	Surface Process	Glass Penetration Model		
		1	2	3
1	$Cs^+(aq)$ reacts with fixed number of glass surface sites to yield diffusing species, $Cs(s)$	Simple diffusion	--	--
2	$Cs^+(aq)$ reacts with time-dependent number of glass surface sites to yield diffusing species, $Cs(s)$	Simple diffusion	Inter-diffusion	Double diffusion

5

II. MATHEMATICAL DEVELOPMENT

In this section the two possible chemical processes for the phase-boundary reaction to be investigated are described and their PDEs are formulated. The first process supposes that aqueous Cs, Cs(aq), reacts with unoccupied glass surface sites, G, to yield a Cs species, Cs(s), that penetrates into the glass via simple one-dimensional diffusion. The initial concentration of reaction sites on the glass surface is a constant, $[G]^0$. Simple diffusion represents the most elementary diffusion model. It would be expected to be valid in cases where the penetrating species do not interchange with components of the glass. Also, it may be found to be valid in self-diffusion situations, e.g. where Na diffuses in a Na silicate glass. Simple diffusion has been successfully used to model diffusion of various species into glasses.[9-12]

Equation (1) shows the surface reaction considered:

$$Cs(aq) + G \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} Cs(s) \tag{1}$$

The equilibrium constant, K_{eq}, is the ratio of the forward reaction-rate constant, K_1, to the reverse reaction-rate constant, K_{-1}. The general one-dimensional diffusion equation for the concentration of a species A, $[A]$, is

$$\frac{\partial [A]}{\partial t} = D_A \frac{\partial^2 [A]}{\partial x^2} \tag{2}$$

with D_A being the diffusion coefficient of the A species.

The PDE for this first process is

$$\frac{\partial [Cs(s)]}{\partial t} = D \frac{\partial^2 [Cs(s)]}{\partial x^2} + K_1 [Cs(aq)]\{[G]^0 - [Cs(s)]\} - K_{-1} [Cs(s)] \tag{3}$$

7

with D being the diffusion coefficient of the penetrating species. A single-boundary condition, the solution concentration of Cs(aq), must be specified, while at time t = 0, [Cs(s)] is equal to zero for all positions x within the glass. The solution volume is assumed to be large enough so that the concentration of Cs(aq) remains constant during the time periods of interest. To constrain the reaction in Eq. (1) to only the glass surface, K_1 and K_{-1} are zero everywhere except at the glass surface, where x = 0. This is justified because Cs(aq) is present only at the surface of the glass. This simple modeling of the first process is sufficient to demonstrate its inability to explain the observed experimental data. Consequently, more sophisticated penetration models for this process were not developed.

The second process considered supposes that the number of reaction sites on the glass surface is time-dependent. The number of active surface sites increases as a function of time because of the exposure of the glass to the aqueous solution. While the exposure times of interest are not sufficient for the etching process to remove significant layers of glass, it is known that even brief exposure to aqueous solution can alter the glass surface.[4] Once an active site has been formed, a Cs(aq) rapidly comes in contact with it, forming the penetrating species Cs(s). Consequently, in this process the rate-limiting step in the formation of Cs(s) is the generaton of active sites rather than, as in the previous process, the reaction of Cs(aq) to form Cs(s).

Several chemical reactions are needed to describe this process. The increasing surface-site concentration is described by

$$G(NA) \xrightarrow{K_1'} G(A) \tag{4}$$

with G(NA) representing nonactive surface sites, G(A) being the reactive glass sites, and K_1' being a rate constant for this reaction. The surface activation process may in reality be a complicated series of reactions depending on solution constituents. For simplicity, it is modeled as a simple irreversible reaction. The rapid reaction of Cs(aq) is given by

$$Cs(aq) + G(A) \xrightarrow[\text{rapid}]{} Cs(s) \tag{5}$$

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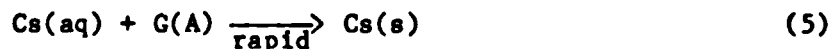
The rate of Cs(s) formation at the surface is specified by the rate equation

$$\frac{d[G(A)]}{dt} = K_1^{\prime} \left\{ [G(NA)]^0 - [G(A)] \right\} = \frac{d[Cs(s)]}{dt} \tag{6}$$

with $[G(NA)]^0$ being the initial number of nonactive sites or, equivalently, the maximum possible number of active sites. Equation (6) may be solved directly to yield

$$[G(A)](t) = [G(NA)]^0 \left[1 - \exp(-K_1^{\prime} t) \right] = [Cs(s)](x = 0) \tag{7}$$

with $[Cs(s)](x = 0)$ representing the surface concentration of Cs(s).

As a first approach, the penetration of Cs(s) into the glass may be modeled by simple diffusion, assuming a constant diffusion coefficient, yielding the PDE

$$\frac{\partial[Cs(s)]}{\partial t} = D\frac{\partial^2[Cs(s)]}{\partial x^2} + K_1^{\prime} \left\{ [G(NA)]^0 - [G(A)] \right\} \tag{8}$$

with $[G(A)]$ specified by Eq. (7). *This model is most similar to the analysis carried out be Franek et al.*

Solutions of Eq. (8) were similar to the experimental data. Consequently, more complicated penetration models were developed for this possible phase-boundary reaction process. The second penetration model considered for this process again uses Eqs. (4) and (5) for the surface reaction. However, the Cs penetration into the glass is assumed to occur by an interdiffusion mechanism. In this model, for each Cs (typically assumed to be in an ionic form) diffusing into the glass, an ion within the glass diffuses back into the solution. Generally, it would be expected that alkali ions within the glass would be the back-diffusing species.[5,13,14] The interdiffusion process has been particularly effective in describing the exchange of ions in solution, such as Na^+, H^+, and Ag^+, with ions in the glass.[5,13-16] One aspect of this model is that the diffusion coefficient depends on the concentrations of the various interdiffusing ions within the glass. Since these concentrations vary

9

with penetration depth, the diffusion coefficient, referred to as the inter-diffusion coefficient, is position-dependent. The resulting PDE cannot be solved in closed form.

For interdiffusion, the diffusion equation takes the form (see, for example, Doremus, Ref. 8).

$$\frac{\partial [A]}{\partial t} = \frac{\partial}{\partial x} \widetilde{D} \frac{\partial [A]}{\partial x} \tag{9a}$$

with $\widetilde{D}$, the interdiffusion coefficient, given by

$$\widetilde{D} = \frac{[T]D_A}{(\frac{D_A}{D_B} - 1)[A] + [T]} \tag{9b}$$

D_A and D_B are the self-diffusion coefficients of the penetrating ion A, and the back-diffusing ion B, respectively. The total concentration of A and B, which is equal to the B concentration at $t = 0$, is indicated by $[T]$.

The resulting PDE to be solved is

$$\frac{\partial [Cs(s)]}{\partial t} = \frac{D_{Cs}}{1 + \frac{[Cs(s)]b}{[T]}} \quad \frac{\partial^2 [Cs(s)]}{\partial x^2}$$

$$- \frac{b[T]D_{Cs}}{([T] + [Cs(s)]b)^2} \left(\frac{\partial [Cs(s)]}{\partial x}\right)^2$$

$$+ K_1^* \{[G(NA)]^0 - [G(A)]\} \tag{10a}$$

with

$$b = \frac{D_{Cs}}{D_B} - 1 \tag{10b}$$

10

The final penetration model to be considered for this process treats the possibility of glass penetration by multiple diffusion paths. A number of authors have experimentally observed what appears to be alkali diffusion via multiple pathways. Frischat[17] has been able to fit Na penetration profiles in several alkali-silicate and alumino-silicate glasses to models using two independent diffusion pathways. Similiarly, "double-diffusion" mechanisms were believed responsible for Na penetration profiles observed by Schaeffer and Mecha[18] in high-silica-content glasses. Lim and Day[19] also found that a multiple-diffusion mechanism yielded the best agreement with their experimental Na diffusion profiles. They specifically discussed penetration in terms of vacancy and interstitialcy mechanisms. In light of experimental evidence indicating multiple diffusion pathways for Na penetration, it was felt that similiar mechanisms for Cs penetration should be considered.

To model a double-diffusion process, two different active glass sites, G^1 and G^2, are formed via

$$G^1(NA) \xrightarrow{K_1'} G^1(A) \tag{11a}$$

and

$$G^2(NA) \xrightarrow{K_2'} G^2(A) \tag{11b}$$

Each of the two types of active sites is assumed to rapidly acquire Cs, forming two independently diffusing species, $Cs^1(s)$ and $Cs^2(s)$. Two different diffusion coefficients, D_1 and D_2, characterize the diffusion of these species. Each of these diffusion processes has been treated as simple diffusion. For this penetration model, two coupled PDEs, Eqs. (12a) and (12b), are obtained:

$$\frac{\partial [Cs^1(s)]}{\partial t} = D_1 \frac{\partial^2 [Cs^1(s)]}{\partial x^2} + K_1' \left\{ [G^1(NA)]^0 - [G^1(A)] \right\} \tag{12a}$$

$$\frac{\partial [Cs^2(s)]}{\partial t} = D_2 \frac{\partial^2 [Cs^2(s)]}{\partial x^2} + K_2' \left\{ [G^2(NA)]^0 - [G^2(A)] \right\} \tag{12b}$$

11

It would have been straightforward to treat each as an interdiffusion mechanism. However, incorporation of the interdiffusion mechanism would require the specification of additional parameters. Considering the limited quantity of data to be analyzed, this was not considered practical.

These PDEs may be solved approximately by using standard finite-difference techniques.[20,21] Briefly, the glass is treated as a semi-infinite, one-dimensional slab. During the exposure times of interest, Cs penetrates only a limited distance into the glass. Consequently, a finite grid in both position x and exposure time t may be used. The grid-point spacing for position and time are, respectively, Δx and Δt. Within this grid system it is possible to approximate derivatives by finite differences. Denoting the value of Cs concentration at the grid point corresponding to $x = i\Delta x$ and $t = j\Delta t$ by $U_{i,j}$, the simple derivative formulas are

$$\frac{\partial U}{\partial t} = \frac{U_{i,j+1} - U_{i,j}}{\Delta t} \tag{13a}$$

$$\frac{\partial U}{\partial x} = \frac{U_{i+1,j} - U_{i,j}}{\Delta x} \tag{13b}$$

$$\frac{\partial^2 U}{\partial x^2} = \frac{U_{i-1,j} - 2U_{i,j} + U_{i+1,j}}{\Delta x^2} \tag{13c}$$

Substitution of these expressions into each PDE results in an "explicit" system of algebraic equations for U at each grid point. The system is explicit in the sense that if all values of $U_{i,j}$ for a specific $t = j\Delta t$ are known, values of each $U_{i,j+1}$ may be solved for individually.

While implementation of these methods is straightforward for process 2, certain complications arise for process 1. In process 1, Cs(aq) reacts with a fixed number of surface sites to yield the diffusing species, Cs(s). In terms of the numerical solution, this process is assumed to be composed of three discrete substeps, each of which occurs during a single time increment, Δt.

12

First, Cs(aq) undergoes the surface reaction. The second and third terms on the right-hand side of Eq. (3) account for this, essentially generating a time-dependent boundary condition for the diffusion portion of the equation. The second substep during Δt is the diffusion of the Cs(s), generated at the surface, into the glass. It is crucial to note that diffusion of Cs(s) away from the surface reduces the Cs(s) concentration at the surface. (This is in contrast to process 2, where the reaction of Cs(aq) is assumed to be rapid enough to immediately replenish the surface concentration.) Consequently, the third substep is the reduction of the Cs(s) surface concentration as a result of diffusion. The amount of Cs(s) that has diffused into the glass during Δt is the difference between the amount prior to and after Δt. This amount of Cs(s) must be removed from the surface layer. A reasonable approximation to process 1 is provided by this scheme.

The power of these finite-difference techniques lies in their ability to solve directly the PDEs resulting from complicated mechanisms. The mechanisms analyzed here are relatively simple, a result of limited experimental data. Within this formalism, though, significantly more complicated mechanisms may be studied. It is a straightforward process to generalize to additional components, interactions between components within the glass, more involved surface reactions, etc.

13

III. INTERPRETATION OF EXPERIMENTAL DATA AND COMPUTATIONAL PROCEDURES

The experiments performed by Franek et al.[7] consisted of immersing glass samples in CsCl solutions at 90°C for various periods of time. Penetration profiles were obtained by using a secondary-ion, mass-spectrometric, neutral-particle-beam technique. To reanalyze the experimental data, the Cs_2O concentration profiles represented in Fig. 1 of their paper for exposure times of 10, 30, 60, and 85 min were digitized with a Hewlett-Packard 9825T mini-computer. Errors due to digitization are less than the size of the symbols representing the data points and much less than the experimental errors indicated in Fig. 2 of their paper.

For comparison of the experimental data with the models described previously in this report, the Cs_2O concentration profiles in Franek et al.'s paper given in terms of mol% were converted to units of atoms/cm^3 by using the indicated composition of the technical glass used. In addition, the aqueous Cs concentration, Cs(aq), was 6×10^{20} ions/cm^3, whereas the total alkali ion content [T] in this glass, a necessary parameter in the interdiffusion model, was determined to be 7.2×10^{21} ions/cm^3.

To solve the PDEs with the finite-difference technique, solutions were calculated over a penetration depth of 25 nm, with a grid point spacing equal to 0.25 nm. The time step was typically 1 s. If the time step was made too large, the method became unstable and the solution rapidly diverged. The finite-difference equations were solved with a Hewlett-Packard 9825T mini-computer. Solutions for exposure times up to 5100 s typically required about 4 h of computer time.

When fitting the experimental data to the computer-generated solutions, there are several free parameters to be specified. For process 1, values are needed for the surface reaction rate constants K_1 and K_{-1}, the surface site concentration $[G]^0$, and the diffusion coefficient D. The surface-reaction rate constants specify how rapidly Cs builds up on the glass surface, whereas the diffusion constant describes how rapidly the Cs penetrates the glass. The

fits were found to be sensitive to values of K_1 but relatively insensitive to K_{-1}. This is due to the short time regimes studied. Over these time periods, insufficient Cs(s) is formed to make the reverse reaction rate very significant. Consequently, the fits were not very sensitive to variations in the ratio of K_1 to K_{-1}, the surface-reaction equilibrium constant, when K_{-1} was changed. Typically, K_{eq} was set at 5×10^{-17} cm^3/atom, indicating that at complete equilibrium most surface sites would be filled. K_{eq} could be varied several orders of magnitude by changing K_{-1} without disturbing the fit. $[G]^0$ and K_1 are found to be the important parameters in attempts to fit the surface concentration. Adjustment of D varies the penetration profile.

In the case of process 2 with a simple-diffusion penetration model, the site-activation rate constant K_1', the maximum surface-site concentration, $[G(NA)]^0$, and D must be specified. For this process, the important parameters for modeling the surface concentration are found to be $[G(NA)]^0$ and K_1'. By varying $[G(NA)]^0$, one produces a range of K_1' values resulting in good fits, although for a given $[G(NA)]^0$ only a single K_1' yields the best fit. This ambiguity might have been resolved if additional data had been taken for somewhat longer periods of time. As exposure time increases, the Cs concentration at the glass surface begins to saturate. Observation of this saturation would allow unambiguous determination of K_1' and $[G(NA)]^0$. Our criterion was to find the minimum surface-site concentration for which K_1' could be adjusted to yield a good fit. Although this ambiguity exists, it does not affect our results with regard to the most significant surface-boundary reaction model. The diffusion coefficients were easily adjusted to match the experimental penetration profiles. The parameter set obtained for the simple-diffusion penetration model formed the core of the parameter sets used in subsequent penetration modeling. Generally, ten computer solutions were required to optimize the parameter set for each model.

IV. RESULTS AND DISCUSSION

Calculations based on process 1 were unable to match the experimental results while maintaining physically meaningful parameter values. To obtain reasonable agreement between the experimental data and calculation results required a maximum active-site concentration of $[G(NA)]^0 > 1 \times 10^{24}$ sites/cm^3. Since a typical glass atom density would be approximately 1×10^{23} atoms/cm^3, the required density was considered unreasonable. Additionally, even when unrealistic parameter sets are employed, process 1 results do not agree with the data as well as process 2 results using realistic parameters. These calculations indicate that it is highly unlikely that the phase-boundary reaction proceeds via a kinetically limited reaction of Cs(aq) with active surface sites on the glass.

In contrast, results from process 2, the rapid reaction of Cs(aq) with a time-dependent number of surface sites, match experimental data quite well. The general quality of the fits allows detailed modeling of the penetration process. Figures 1 through 3 display the best fits to Franek et al.'s experimental data resulting from each proposed penetration model. Results for reaction followed by simple diffusion are presented in Fig. 1. The diffusion coefficient was found to be 4.5×10^{-17} cm^2/s. The current result is essentially the same as Franek et al.'s[7] value for the diffusion coefficient, 5×10^{-17} cm^2/s. This is reasonable, as the current results are essentially the exact solution of the model previously treated empirically.

Reaction followed by an interdiffusion process is expected to be a more physically realistic model. Two regimes of the interdiffusion process were investigated, $D_B > D_{Cs}$ and $D_B < D_{Cs}$. The best interdiffusion fits were found in the range $5\, D_{Cs} > D_B > 0.2\, D_{Cs}$, with $D_B = D_{Cs}$ yielding the simple diffusion fit. In Fig. 2 we present representative fits for both interdiffusion regimes. For $D_B = 0.2\, D_{Cs}$, D_{Cs} was found to be 1×10^{-16} cm^2/s, whereas for $D_B = 5\, D_{Cs}$, D_{Cs} was found to be 3.4×10^{-17} cm^2/s. Each regime represents a different physical situation. The significance of these regimes will be subsequently discussed.
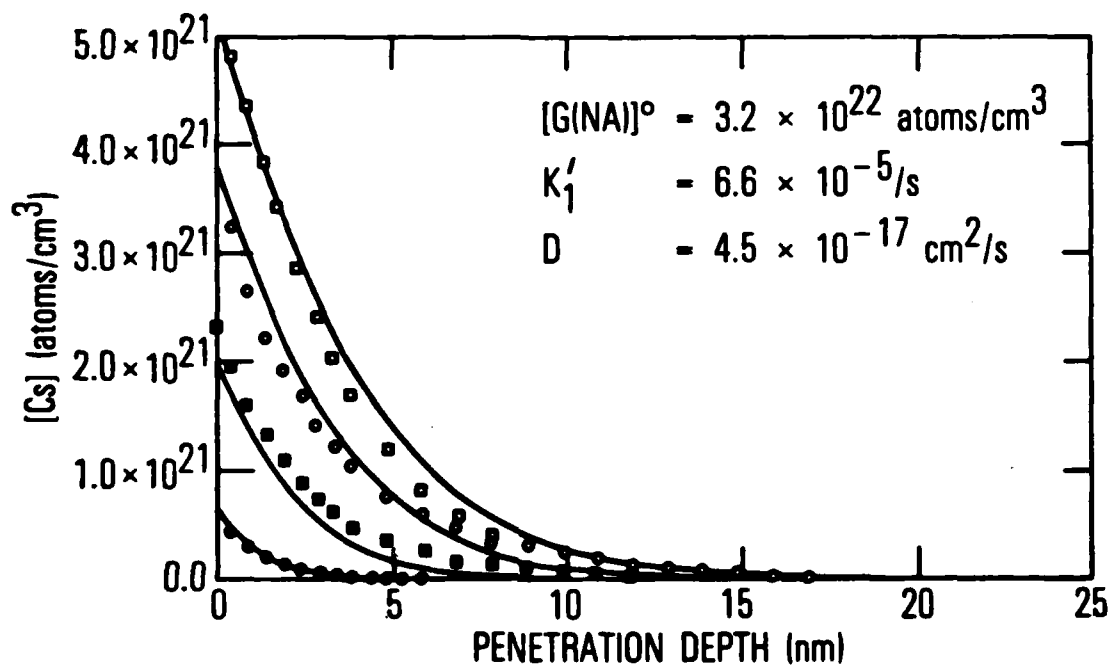
Fig. 1. Cs Penetration Profiles from the Simple Diffusion Penetration Model (solid lines) and Franek et al.'s Experimental Data for Exposure Times of 600 (●), 1800 (■), 3600 (○), and 5100 (□) s
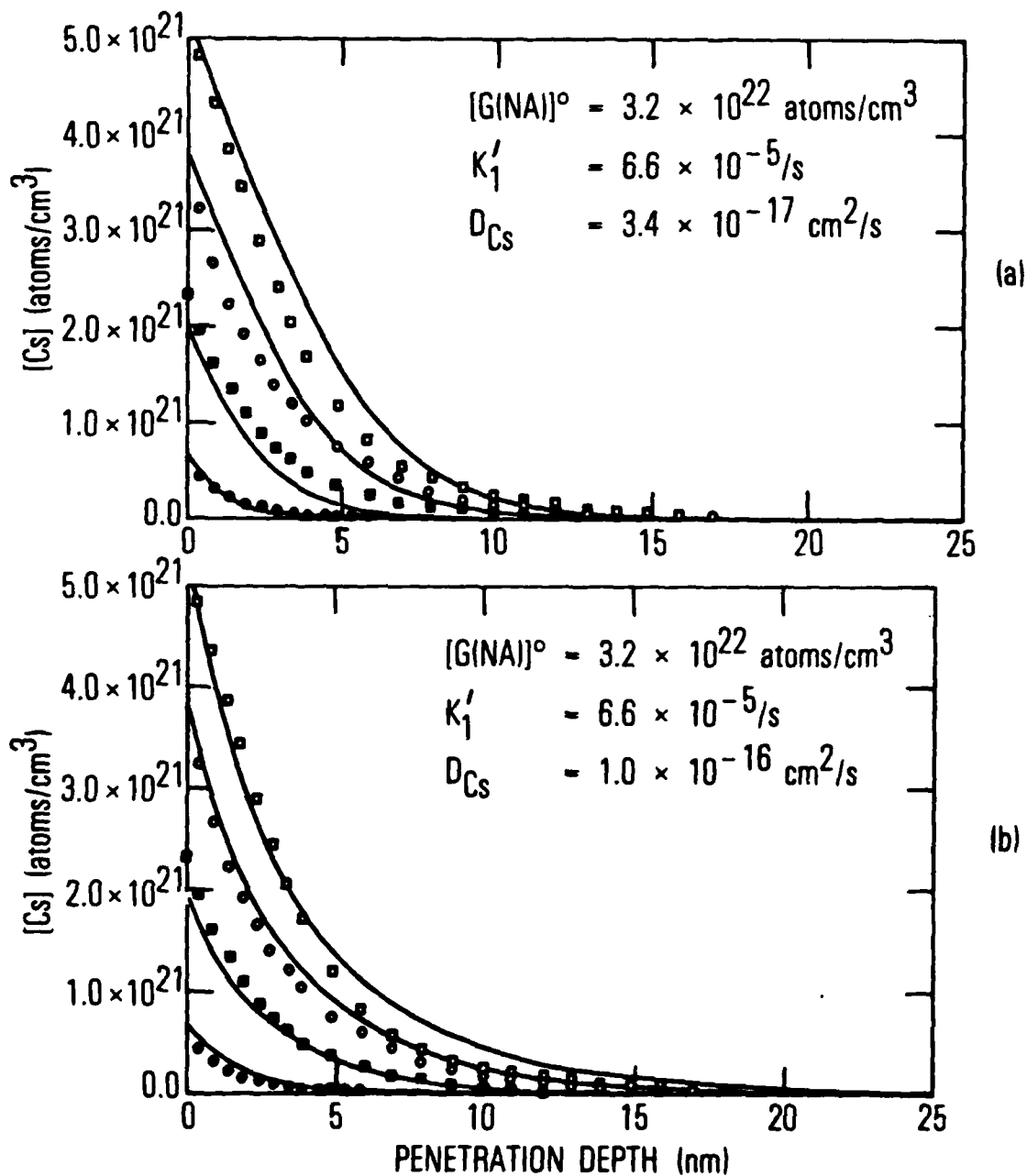
Fig. 2. Cs Penetration Profiles from Interdiffusion
Penetration Models. (a) $D_B = 5 \ D_{Cs}$ and
(b) $D_B = 0.2 \ D_{Cs}$ are given by solid lines.
Experimental data are as in Fig. 1.

19

(a)

$[G^1(NAI)]^\circ = 3.2 \times 10^{22}$ atoms/cm^3

$K_1 = 1.0 \times 10^{-5}$/s

$D_1 = 3.0 \times 10^{-17}$ cm^2/s

[Cs] (atoms/cm^3)

(b)

$[G^2(NAI)]^\circ = 4.0 \times 10^{20}$ atoms/cm^3

$K_2' = 2.5 \times 10^{-3}$/s

$D_2 = 2.0 \times 10^{-16}$ cm^2/s

[Cs] (atoms/cm^3)
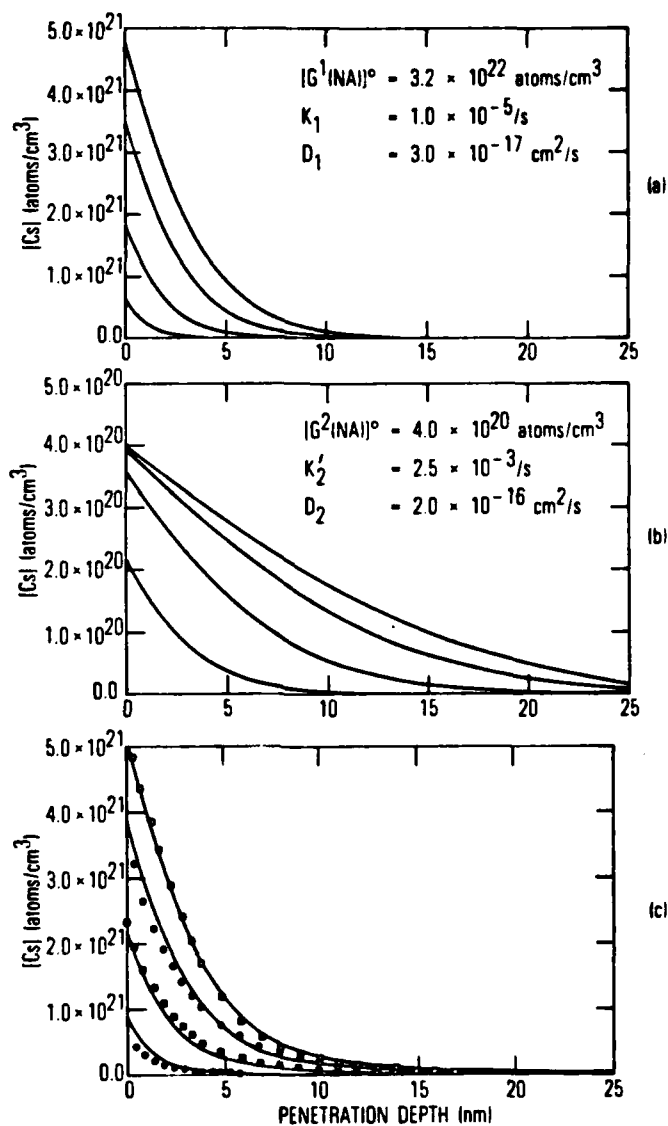
(c)

[Cs] (atoms/cm^3)

PENETRATION DEPTH (nm)

Fig. 3.   Cs Penetration Profiles from the Double-Diffusion
Penetration Model.   (a) Major diffusion pathway,
(b) minor diffusion pathway, and (c) total.
Experimental data in (c) are as in Fig. 1.

Results for the third penetration model, reaction followed by double diffusion, are shown in Fig. 3. The penetration profiles of Cs diffusing by each pathway are shown along with the total Cs penetration profile. The experimental data were best described as the sum of the major process ($D_1 = 3 \times 10^{-17}$ cm^2/s) and the minor process ($D_2 = 2 \times 10^{-16}$ cm^2/s). It is interesting to note that to obtain the best fit to the data, the minor penetration pathway was required to have its surface concentration saturated at an exposure time of ~3600 s. Consequently, a unique pair of values could be found for K_2^- and $[G^2(NA)]^0$, 4.2×10^{-24} cm^3/atom $\cdot$ s and 4×10^{20} atoms/cm^3, respectively. Unfortunately, as noted previously, the main pathway was unsaturated for all exposure times considered, which prevented a unique determination of K_1^- and $[G^1(NA)]^0$.

Can one penetration model be said to describe the experimental results most accurately? Each model yields reasonable agreement with the data for penetration depths less than 5 nm. However, beyond 5-nm penetration depths the fits differ significantly. In Fig. 4 the penetration profiles beyond 5 nm for each model are displayed for comparison. Inspection of Fig. 4 indicates that the double-diffusion mechanism yields the best fit to the experimental data. To quantify the differences in quality of fits, an average absolute percent difference, $\overline{\Delta}$, between the experimental point and the predicted value has been computed for each model. After consideration of all the experimental data, $\overline{\Delta}$'s for double diffusion, interdiffusion ($D_B > D_{Cs}$), simple diffusion, and interdiffusion ($D_B < D_{Cs}$) are respectively 20%, 27%, 50%, and 59%. If only data beyond a 5-nm penetration is considered, the respective $\overline{\Delta}$'s are 25%, 39%, 82%, and 96%. The double-diffusion mechanism shows the best agreement with both the entire set of experimental results and, in particular, with the experimental data beyond 5 nm in depth. Consequently, of the models currently studied, the double-diffusion model appears to explain most accurately the penetration processes occurring within the glass. Of course, this conclusion might not be valid should any significant errors have occurred during the acquisition of the experimental data.
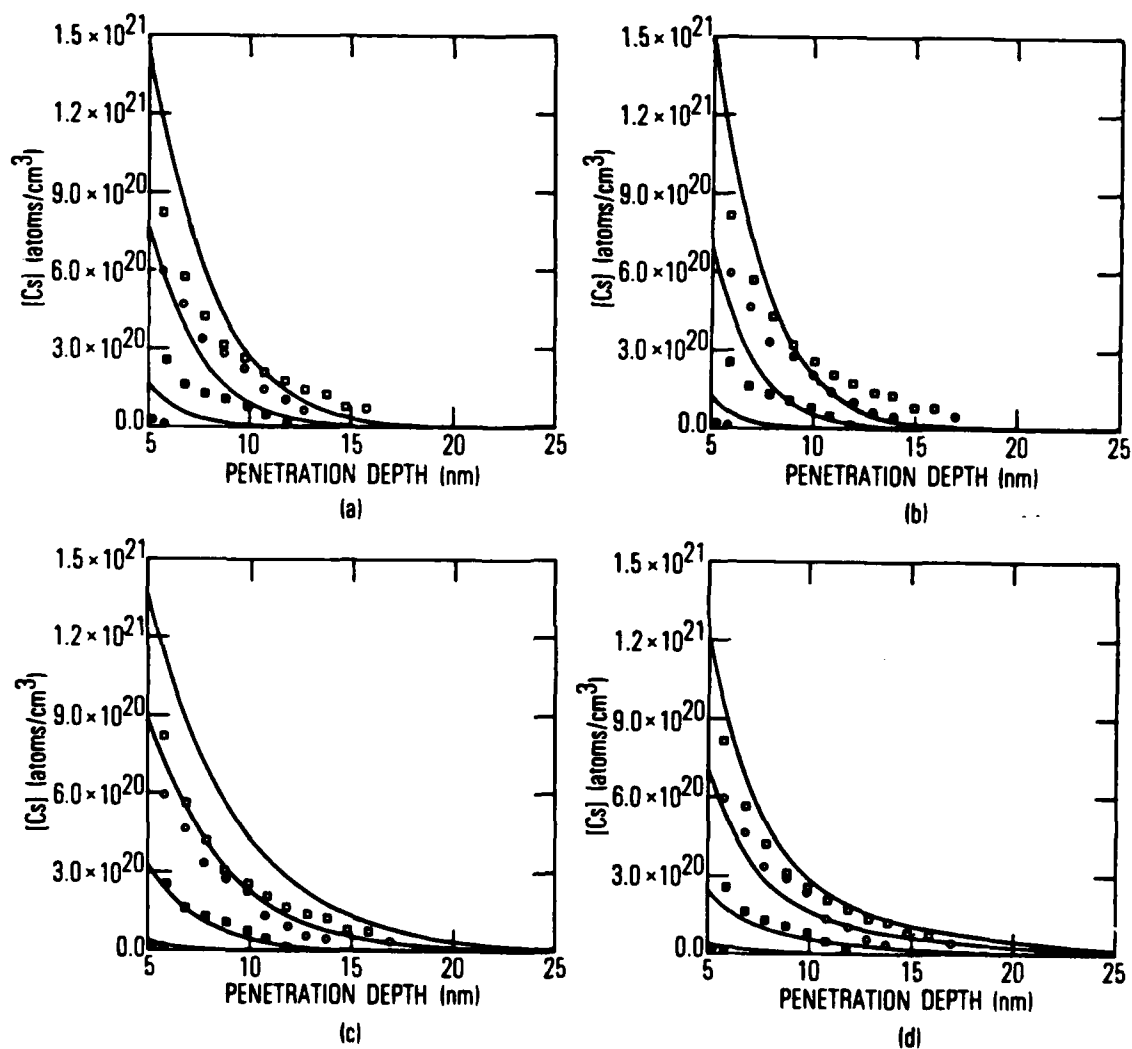
Fig. 4. Cs Penetration Profiles from (a) Simple Diffusion, (b) Interdiffusion ($D_B = 5\ D_{Cs}$), (c) Interdiffusion ($D_B = 0.2\ D_{Cs}$), and (d) Double-Diffusion Penetration Models over Penetration Depths of 5 to 25 nm. Experimental data are as in Fig. 1.

A side aspect is that the model providing the second-best fit is inter-diffusion, with $D_B = 0.2 \, D_{Cs}$. The most reasonable interdiffusion process is the replacement of alkali ions in the glass with Cs ions from the solution. The alkali ions in the glass are Na^+ and K^+, which would be expected to diffuse more rapidly than Cs^+.[16] Consequently, this model, even though it yields reasonable agreement with experiment, should most likely be discounted. A possible reason for the inability of the interdiffusion mechanism to realis-tically describe the Cs penetration process is that D_{Cs} and D_B may be concentration-dependent. Varshneya and Milberg[22,23] have shown that the potassium self-diffusion coefficient for temperatures > 340°C can be concentration-dependent. If experimental self-diffusion coefficient data for the ions, glass type, and temperature under study existed, it would have been straightforward to incorporate them expicitly into the finite-difference model. In the absence of these data, these coefficients were treated as concentration-independent.

With the observation of a double-diffusion process, it would be desirable to identify what microscopic mechanisms are responsible for each diffusion pathway. The present studies do not directly address this point. However, in the light of previous studies, *some speculation is possible*. Lim and Day[19] found that two principal diffusion mechanisms occur when Na diffuses into Na, K, or Rb silicate glasses. The first is the vacancy mechanism, in which a single penetrating ion jumps from lattice vacancy to lattice vacancy. Interstitialcy, the second mechanism, is a two-atom process. A penetrating ion initially in an interstitial site jumps to a lattice site, displacing the ion at that site to another interstitial site. In their experiments, Lim and Day found that the interstitialcy mechanism dominates at low temperatures (T < 300°C), whereas at higher temperatures the ions diffused via the vacancy mechanism. Although the effects of glass composition and differing experi-mental conditions on the diffusion mechanisms are not clear, a simple extrapo-lation of these results to Franek et al.'s conditions would indicate that the major diffusion mechanism would be interstitialcy. Consequently, a reasonable speculation is that this mechanism is the major diffusion mechanism observed. The minor mechanism would similiarly be expected to be the vacancy mechanism.

Finally, we note that to really test a particular phase-boundary reaction and penetration mechanism, additional experimental data are required. As was stated previously, somewhat longer exposure times would allow unique determination of the surface-site rate constant and the glass-surface-site concentration used in the present modeling. Additionally, performing experiments at a variety of aqueous Cs concentrations would allow more detailed investigation of the surface reactions. More complicated reaction mechanisms could then be formulated and tested.

V. CONCLUSIONS

This report demonstrates how effectively model processes may be compared to experimental data through the direct solution of the resulting PDEs by using a simple finite-difference technique. The capability to test a variety of model processes is important for several reasons. By investigating different models, one gains insights into the actual processes occurring within the glass, including microscopic aspects of the reaction and subsequent penetration. Additionally, parameters extracted from the experimental data, e.g. diffusion coefficients, were found to be model-dependent; consequently, to obtain their proper values, one must use the correct model. Specifically, processes differing in surface reactions have been applied to the phase-boundary reaction data of Franek et al. The experimental data are entirely consistent with the rapid reaction of aqueous Cs^+ with a time-dependent number of surface sites. The required increase in surface-site concentration with time is believed to occur through reactions between the glass surface and the aqueous solution. Subsequent penetration of Cs into the glass was more accurately modeled by a double-diffusion mechanism.

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