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Silica in humid air environment

(I): Diffusion in the absence of stresses

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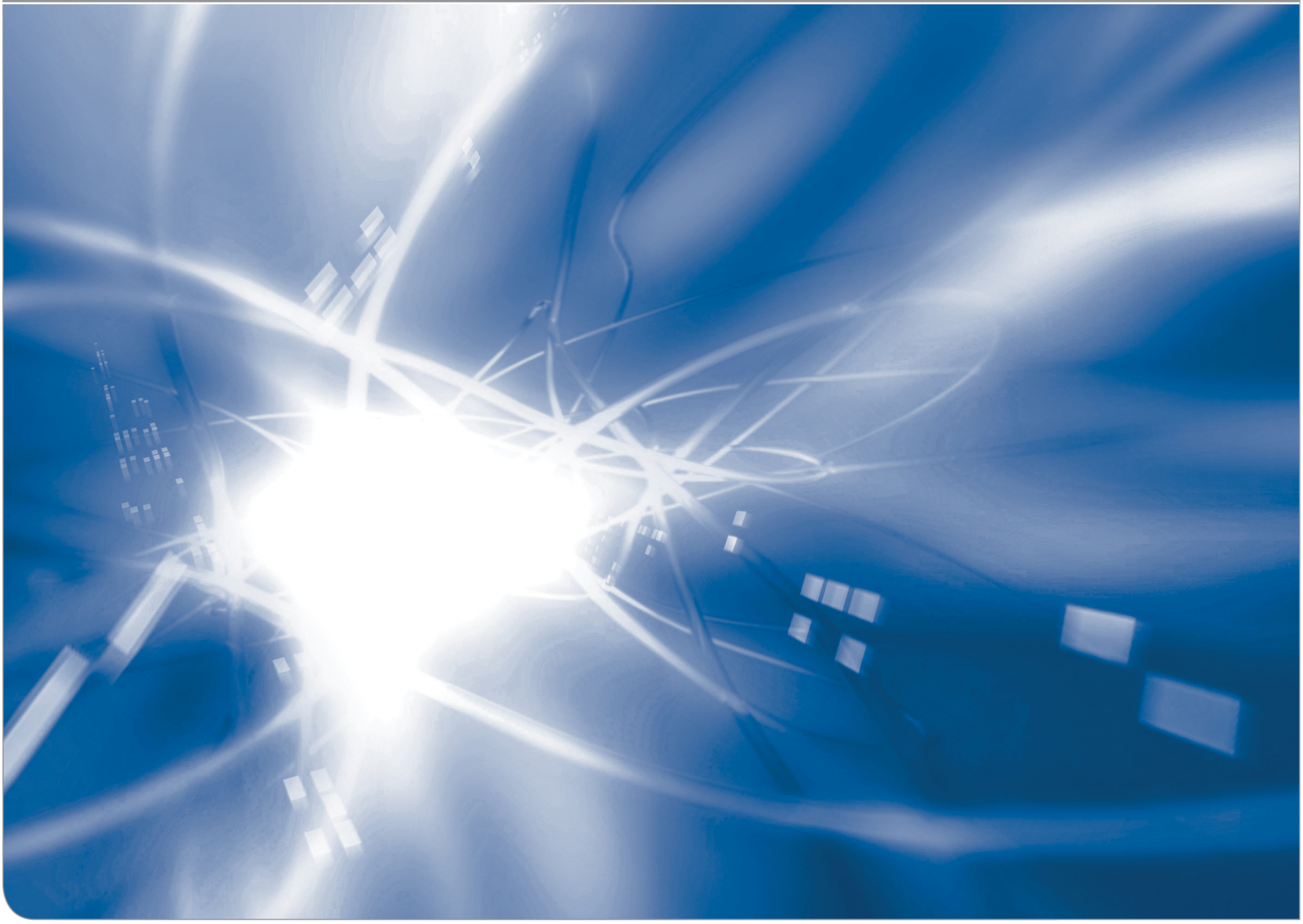
KIT SCIENTIFIC WORKING PAPERS **11**



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Abstract

Water diffusion into silica glass results in a zone near the surface of the glass consisting of a mixture of water and ≡SiOH dissolved in the unreacted silica glass. The relative amount of water and ≡SiOH in the glass structure is controlled by the appropriate equilibrium constant of reaction between the water and the glass. Water added to silica glass increases its specific volume so that the silica expands and the volume near the surface is larger than it was before being penetrated by the water. As the bulk material beyond the zone of water penetration suppresses free expansion of the glass, biaxial compressive swelling stresses develop near the surface as a consequence of water penetration. These stresses can play a significant role in influencing the strength of silica glass and its sensitivity to water as a stress corrosion agent.

The development of the diffusion zone depends significantly on whether the water is present as a liquid, or as a component of a gaseous environment. As a liquid, the diffusion equation used to describe the development of the water penetrated zone near the surface of the glass treats the problem as if the surface of the glass was saturated with water from the start of the exposure. In gaseous environments having a high concentration of water vapor, the surface water concentration was found to be time-dependent. The gaseous diffusion problem is by far the more complex problem to describe.

Detail aspects of diffusion in gases must include:

(I) Effects of rising surface concentration on diffusion.

(II) Effects water diffusion on swelling of the glass.

(III) The influence of water diffusion on strength and deformation under an external load.

The present report deals with Point I of the gaseous diffusion problem.

Contents

DIFFUSION BEHAVIOUR IN THE ABSENCE OF STRESSES

1. Water diffusion

1.1 Surface concentration

Water, H_2O (*l*), in contact with silica glass surfaces diffuses into the glass and reacts with the silica network as follows:

$$\equiv\text{Si-O-Si}\equiv + H_2O \leftrightarrow \equiv\text{SiOH} + \text{HOSi}\equiv \tag{1}$$

Due to diffusion, concentrations of both molecular water, $C = [H_2O_m]$, and hydroxyl water, $S = [\text{SiOH}]$, decrease with increasing distance, z, from the glass surface. If the reaction given by Eq. 1 is in equilibrium, the diffusion process is governed by the diffusion differential equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \tag{2}$$

where D is the effective diffusivity that takes into account the chemical reaction given by Eq. 1 [1]. The diffusivity has an Arrhenius type of temperature dependence.

Solution of the diffusion equation requires an appropriate boundary condition to be chosen, very often a constant surface concentration of water:

$$C(z = 0, t) = C_0 = \text{constant} \tag{3}$$

For a semi-infinite body, this assumption results in the following equation as a solution of the diffusion equation, *i.e.*, Eq. 2:

$$C = C_0 \text{erfc}\left(\frac{z}{2\sqrt{D\,t}}\right), \tag{4}$$

which is well established for liquid water as the environment [2].

In the case of water vapor as the environment, the behavior of water at the silica interface does not follow Eq. 3. Experimental results show that the concentration of water is not a constant at the surface, but increases continuously with time, until it reaches the solubility limit of water in the silica glass [3, 4].

1.2 Results by Oehler and Tomozawa [5]

Figure 1a shows both the molecular water and hydroxyl water concentrations of silica glass at the surface (z = 0) for a temperature of 250°C and a vapour pressure of 39 atm [5]. The fact that the equilibrium ratio between ≡SiOH and H_2O are achieved in these experiments is supported by the fact that the ratio, S/C, slightly below 3 is reached after a relatively short exposure time, ~200 h, Fig. 1b. However, the fact that

C_0 has not achieved a constant value in Fig. 1a suggests that the solubility limit of water in the glass has not been realized.

The experimental results in Fig 1a [5] for $C(z=0,\, t)$ are a clear contradiction of the assumption of a constant surface value for the water concentration. So, one cannot assume that the surface concentration of water stays constant under the conditions used for the experiment. There is an incredible agreement with the thermal analogue of thermal shock behaviour under heat transfer boundary conditions, governed by a heat transfer coefficient. This calls for a surface condition

$$\frac{dC}{dz}=\frac{h}{D}(C_0-C) \quad \text{at } z=0, \tag{5}$$

where C_0 is the content of molecular water reached at $z=0$ for $t\to\infty$.

The parameter h may be interpreted as either

- a *mass transfer coefficient* for diffusion, *i.e.* there exists a barrier to the transport of water across the surface of the glass,
- or, following the suggestion by Doremus [6, Section 4.7], the *reaction parameter* for a slow surface reaction that limits the entrance of molecular water species.

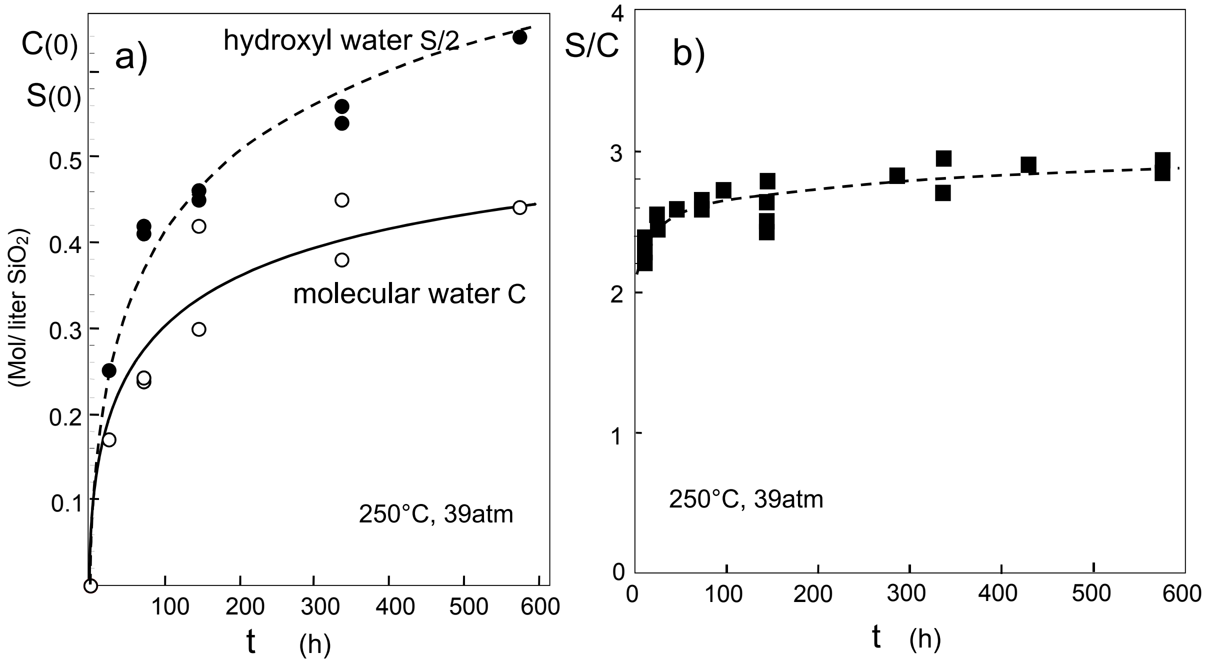

Fig. 1 a) Molecular water (C) and hydroxyl water content ($S/2$) at the surface of silica for 250°C at an equilibrium vapour pressure of 39atm [3] (solid curve: fitted to *I-R* data according to Eq. 7, dashed curve: computed from C and S/C-ratio), b) ratio S/C (results from Oehler and Tomozawa [5]).

As shown by Carslaw and Jaeger [7] (Section 2.7), the concentration profile, *C(z)* resulting from the boundary condition given by Eq. 5 for a semi-infinite body is given by the following equations (the case of a thin sheet is treated in the Appendix):

$$C(z,\,t)/C_0=\operatorname{erfc}\left[\frac{z}{2\sqrt{Dt}}\right]-\exp\left[\frac{h}{D}z+\frac{h^2}{D}t\right]\operatorname{erfc}\left[\frac{z}{2\sqrt{Dt}}+h\sqrt{\frac{t}{D}}\right] \tag{6}$$

and at the surface where z=0:

$$C(0,\,t)/C_0=1-\exp\left[\frac{h^2}{D}t\right]\operatorname{erfc}\left[h\sqrt{\frac{t}{D}}\right], \tag{7}$$

where C_o is the surface concentration as $t\rightarrow\infty$, i.e. $C_0=C(0,t\rightarrow\infty)$.

The C-measurements of Fig. 1a, carried out on specimens of the order of 1mm thick were fitted for the molecular water according to Eq. 7, resulted in the following fitting constants:

$$C_0=0.62\ [0.564,\ 0.68]\ (\text{mol } H_2O/\text{litre } SiO_2),\ h/\sqrt{D}=0.075/\sqrt{\text{h}}\ [0.057,\ 0.092], \tag{I}$$

with the 68% confidence intervals given in brackets. This result is introduced into Fig. 1a as the solid curve.

1.3 Results by Wakabayashi, Davis and Tomozawa [3, 8]

The measurements of Fig. 2 were carried out by Davis and Tomozawa [3] and Wakabayashi and Tomozawa [8] at a temperature of 350°C under 355 Torr water vapour pressure. The specimen widths, $2W$, ranged from 200 µm to 1000 µm. Since the maximum penetration of water was less than 70 µm (Fig. 4a in [3]), the solutions Eqs. 6 and 7 are applicable for the diffusion results. At 350°C, the equilibrium of the S/C-ratio should be reached earlier than in the 250°C tests. Consequently, the S/C should be constant the experiment indicated in Fig. 2. In this case, the hydroxyl distribution and the molecular water distribution can be described by the same equation:

$$\frac{S(z,t)}{S_0}=\frac{C(z,t)}{C_0}, \tag{8}$$

where S_0 is the saturation value of the hydroxyl concentration for $t\rightarrow\infty$.

By curve fitting of Eq. 7 to the data points in Fig. 2, the following parameters were determined:

$$S_0=18.9\ \text{cm}^{-1}\ [12.8,\ 25.0]\cong 2000\ \text{ppm},\ h/\sqrt{D}=0.0315/\sqrt{\text{h}}\ [0.0153,\ 0.0477] \tag{II}$$

The result is introduced in Fig. 2 as the continuous curve.

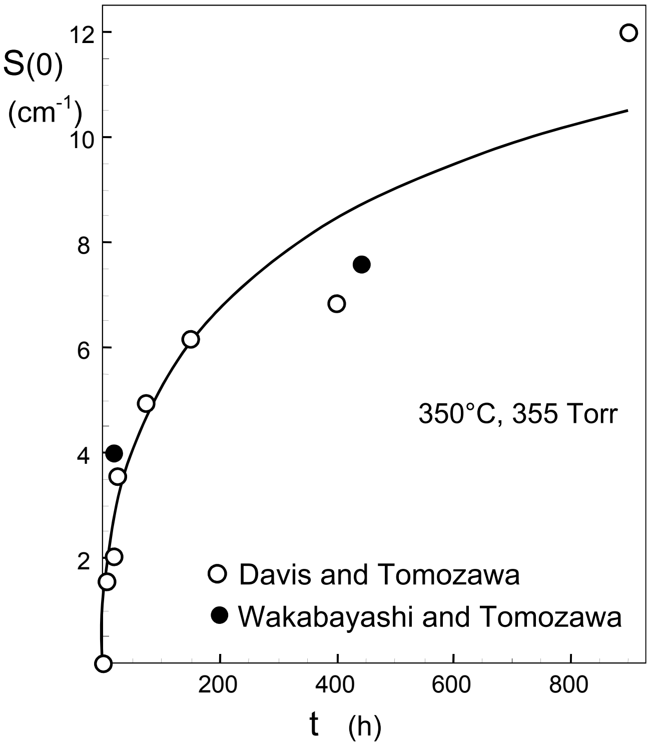

Fig. 2 Hydroxyl surface concentration after hydration at 350°C in water vapour of 355mm Hg) measured by Tomozawa et al.[3, 8], (ordinate scaled in terms of the IR absorption coefficient).

1.4 Results by Helmich and Rauch [4]

For the a temperature of 200°C, surface equilibrium between $C(0)$ and $S(0)$ is not expected in the shorter exposure times of 5-20h reported by Helmich and Rauch. The hydroxyl content at the surface, $S(0)$, develops with time according to Eq. 4.25 in reference [6]:

$$\frac{dS(0,\,t)}{dt} = \chi C(0,\,t) - \mu S(0,\,t) \tag{9}$$

Re-arranging yields a linear differential equation of first order

$$\frac{dS(0,\,t)}{dt} + \mu S(0,\,t) = \chi C(0,\,t) \tag{9a}$$

The two coefficients μ and χ can be related to the equilibrium constant *k* for the *S*/*C*-ratio, the ratio of saturation concentrations

$$\frac{S_0}{C_0} = k \tag{10}$$

From Eq. 9 it follows for $t \to \infty$: $dS/dt=0$, and consequently

$$\chi = \mu \frac{S_0}{C_0} = \mu k \tag{11}$$

With the initial condition $S(0,t{=}0)$, the solution reads

$$\frac{S(0,t)}{C_0}=\frac{k}{\alpha^2+\mu}\left\{\alpha^2+\mu(1-\exp[\alpha^2 t]\mathrm{erfc}[\alpha\sqrt{t}])-\alpha\exp[-\mu t](\alpha+\sqrt{\mu}\,\mathrm{erfi}[\sqrt{\mu t}])\right\} \quad (12)$$

with the abbreviation $\alpha = h/\sqrt{D}$ and the *imaginary error function* erfi.

The total water content C_w is then given by

$$C_w(0,\,t)=C(0,\,t)+\tfrac{1}{2}S(0,\,t)\ ,\ \ C_{w,0}=C_0+S_0/2 \qquad (13)$$

In Fig. 3 the molecular, hydroxyl and total water concentrations at the surface are plotted versus the time. All concentrations are normalized to their saturation values.

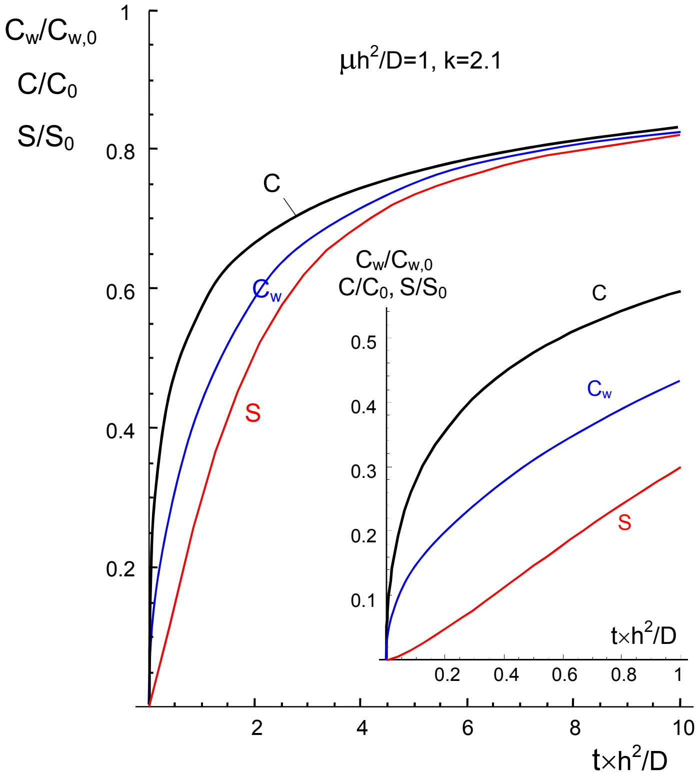

Fig. 3 Surface values of the water species C, S and the total water C_w as a function of time for an equilibrium constant of k=2.1, valid for 200°C, inset with same .

Water concentration measurements were carried out on silica by Helmich and Rauch [4]. The silica specimens were soaked in saturated water vapour at 200°C (15.3 bar).

Figure 4a shows the surface concentration of the water from H-measurements using the technique of Nuclear Reaction Analysis [4]. We therefore fitted the data of Fig. 4a according to Eq. 13 using S_0/C_0=2.1 with the result:

$$C_0=1.71\times 10^{20}\,/\mathrm{cm}^3,\ \alpha=1.902/\sqrt{\mathrm{h}},\ \mu=0.130/\mathrm{h} \qquad \text{(III)}$$

from C_0 we obtain: $S_0=2.1\times C_0=3.42\times 10^{20}\,/\mathrm{cm}^3$, $C_{w,0}=2.05\ C_0=3.51\times 10^{20}\,/\mathrm{cm}^3$.

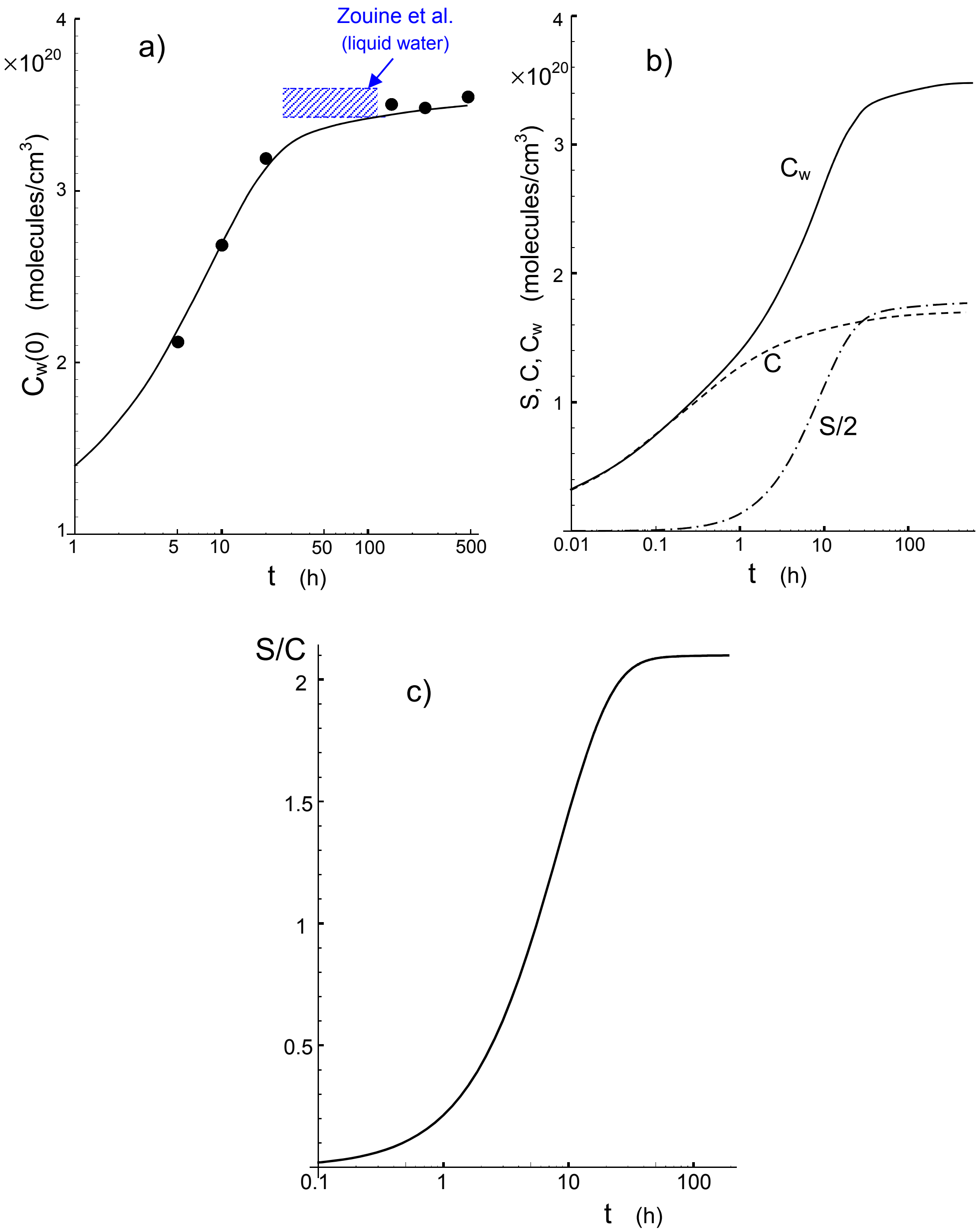

Fig. 4 a) Total water concentration C_w at the surface at a temperature of 200°C in saturated water vapour by Helmich and Rauch [4] (data points), Curve: Eq. 13 fitted to the data, hatched area: Region of measurements by Zouine et al. [2] carried out in liquid water, b) hydroxyl and molecular water concentrations, c) S/C-ratio vs. time.

Since only 6 data points were available for the fitting analysis, and 4 parameters had to be determined, the results do not have high precision. Hence, confidence intervals were not determined.

The two water species, C and $S/2$ are shown in Fig. 4b. Finally, the time-dependent S/C-ratio is represented in Fig. 4d. From this diagram we can expect that equilibrium is reached after about 30 h.

2. Shape parameter $h/\sqrt{D}$ from water uptake

The molecular water uptake per surface unit, m_C, after time t results by integrating the water profile of Eq. 6 from $z=0$ to $z\to\infty$. With the help of Mathematica [9] we obtain

$$m_C = \int_0^\infty C(z)dz = C_0 \frac{D}{h}\left\{\frac{2}{\sqrt{\pi}}\frac{h}{\sqrt{D}}\sqrt{t} - \left(1-\exp\left(\frac{h^2}{D}t\right)\mathrm{erfc}\left(h\sqrt{\frac{t}{D}}\right)\right)\right\} \tag{14}$$

For large values of $h/\sqrt{(t/D_0)}$ the water uptake tends asymptotically to

$$m_\infty \to C_0\left\{\frac{2}{\sqrt{\pi}}\sqrt{tD} - \frac{D}{h}\right\} \tag{15}$$

The time $\sqrt{t_0}$ at which the asymptote coincides with the $\sqrt{t}$ axis is

$$\sqrt{t_0} = \frac{\sqrt{\pi}}{2}\frac{\sqrt{D}}{h} \tag{16}$$

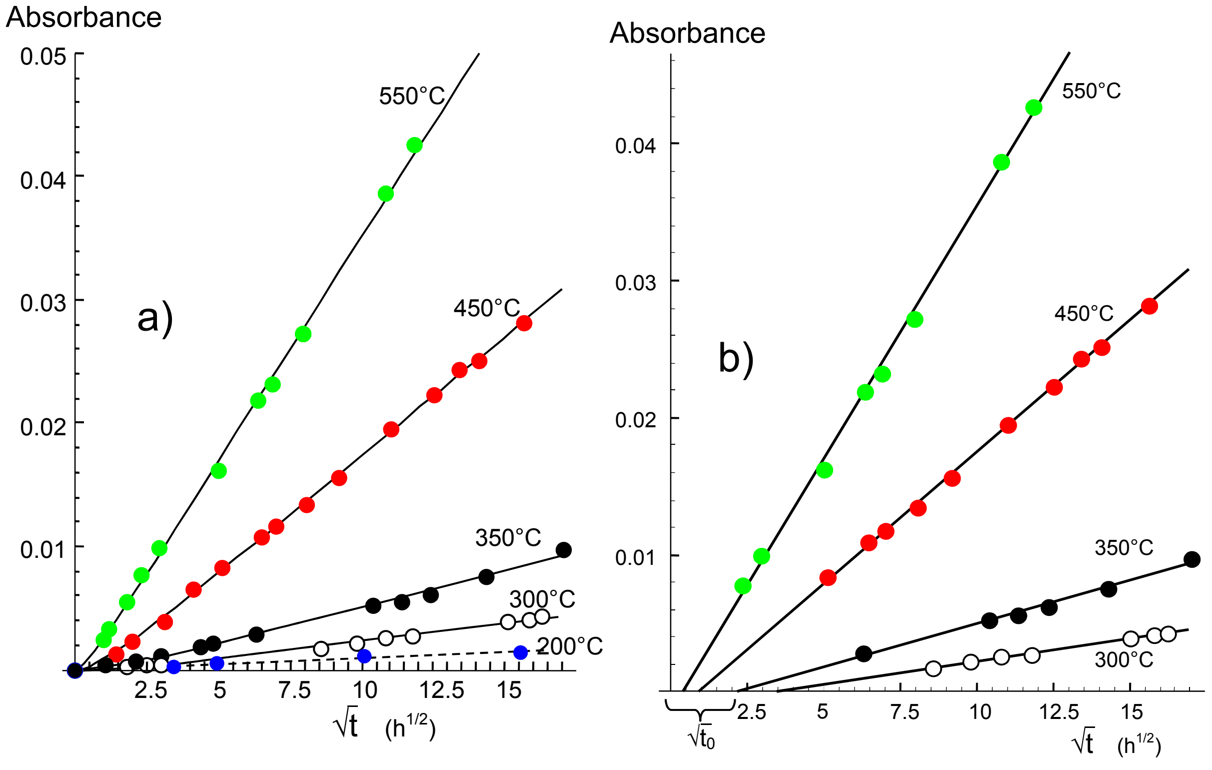

Fig. 5 a) Water uptake of silica by water vapour soaking at different temperatures and water vapour pressure of 355 Torr after Wakabayashi and Tomozawa [8], curves fitted to the data via Eq. 14, b) determination of the asymptotes from results at large times using Eq. 16.

Under the assumption that equilibrium between molecular and hydroxyl water is reached even for short soaking times, Eqs. 14, 15 are valid also for the hydroxyl S.
The uptake measurements by Wakabayashi and Tomozawa [8] for the hydroxyl water S are plotted in Fig. 5 by the solid and open circles.

In a first evaluation, we fitted Eq. 14 to all the data and obtained the curves in Fig. 5a. The fitted-parameters $h/\sqrt{D}$ are plotted in Fig. 6 as the open circles. An evaluation of the abscissa sections $\sqrt{t_0}$ in Fig. 5b via Eq. 16 resulted in the triangles of Fig. 6.

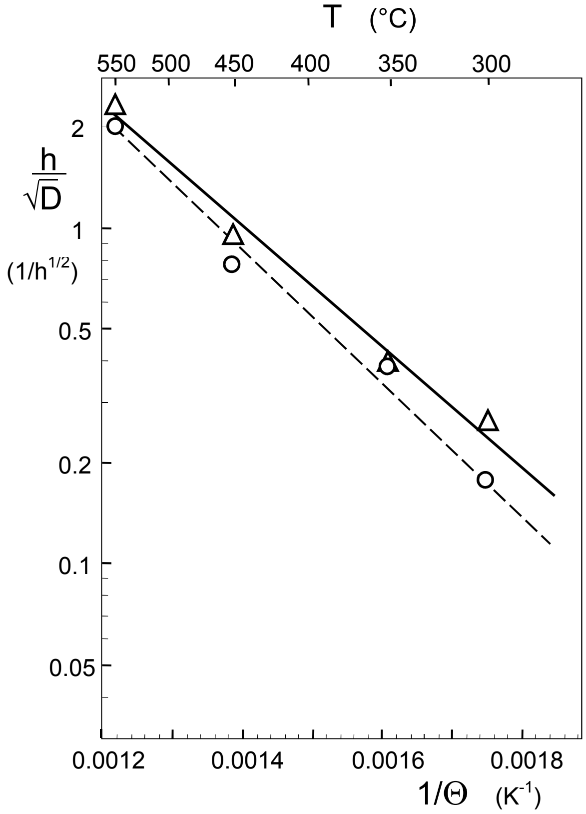

Fig. 6 Parameter $h/\sqrt{D}$ as a function of temperature for constant water vapour pressure of 355 Torr; circles: evaluation of the data in Fig. 5a by fitting to Eq. 14, triangles: results from the asymptotic behaviour via Eq. 16.

The straight lines in this diagram yield

$$\frac{h}{\sqrt{D}} = A \exp\left(-\frac{Q}{R\Theta}\right) \tag{17}$$

with the fitting parameters: A=527 ($1/h^{1/2}$), Q=38.1 (kJ/mol) for the circles and A=306 ($1/h^{1/2}$), Q=34.0 (kJ/mol) for the triangles.

3 Surface concentration for tests in liquid water

Water concentrations in silica glass exposed to liquid water are reported by Zouine *et al.* [2] at temperatures ranging from 25°C to 200°C. For several of the temperatures, the authors measured water content after different times. The ratio of longer to shorter times ranged from about 2 to 4. The related concentrations ratios, $C_{\text{short}}/C_{\text{long}}$, are plotted in Fig. 7 as a function of Temperature.

The mean value was found to be $C_{\text{short}}/C_{\text{long}} = 1.015$ with the standard deviation SD = 0.052. The mean value is represented in Fig. 7 by the dash-dotted line, the region of ±SD by the hatched area. Thus, there is no indication for an increasing ratio of surface water concentration with increased soaking time as there is for water vapor. From this result we can conclude that the results from [2] represent saturation values. Consequently, a constant surface concentration of water and the use of Eq. 4 is justified for the analysis.

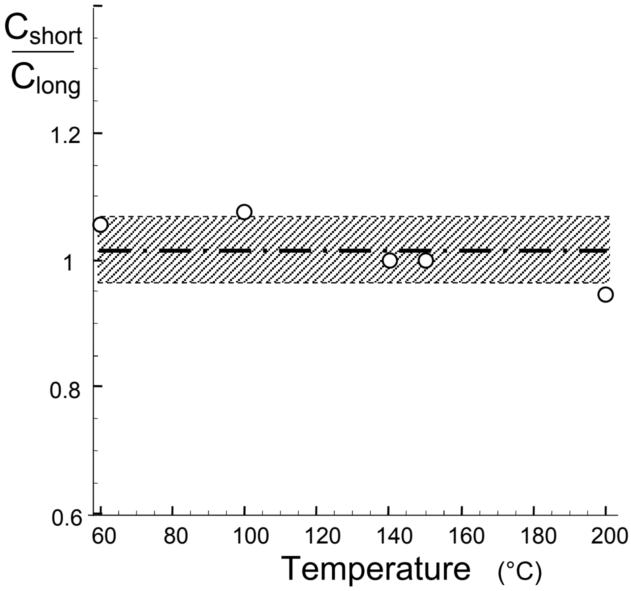

Fig. 7 Ratio of the surface water concentrations for "short" and "long" soaking times from Zouine et al. [2]; dash-dotted line: mean value, dashed lines: ±standard deviation.

4 Discussion

In the opening sections of this paper we commented on the fact that whereas silica glass soaked in water behaves as if the surface concentration of water in the glass was a constant, in water vapour, the diffusion process behaves as if there were a barrier to water transport at the surface of the glass. The physical basis of the barrier lies in the nature of the glass surface and the chemical processes that occur at that surface during the diffusion, and can be an actual physical barrier that slows the passage of water molecules, or a reaction parameter for a slow surface reaction that limits the entrance of water molecular species to the glass. In either case, the details of the chemistry at the glass surface have to be understood. In this section, we speculate on possible mechanism that can account for the physical observations.

The chemistry of the structure of silica glass surfaces has been reviewed in some detail by Iler [10], and by Holland [11]. The facts that seem to be most significant in the present study is that silica glass surfaces in a normal atmospheric environment is covered with silanol groups, ≡SiOH, and these in turn have water molecules, two to each silanol, attached to them, held on by hydrogen bonding. In air, depending on the humidity, additional layers of water can be attached to the surface of the glass.

Surfaces covered with silanol groups are easily wetted by water; the surfaces are hydrophilic.

Water can be entirely removed from the surface of silica glass by heating the glass to temperatures in excess of 1000°C. Water is eliminated by the reaction,

$$2 \equiv SiOH \rightarrow Si\text{-}O\text{-}Si + H_2O, \qquad (18)$$

i.e., the reverse of Eq. 1. Then the surfaces are covered with siloxane groups, Si-O-Si. Any $\equiv$SiOH groups remaining in the glass are confined to the interior of the glass where evaporation of the H_2O is difficult. Rehydration of such surfaces is difficult. Water usually beads up on the surface, rehydration taking some time when exposing the surface to water. Siloxane covered surfaces provide a natural barrier to the penetration of water into the bulk of the glass, and the time to rehydration could account for the time required for the surface to become saturated with water.

The above scenario does not apply to the present situation at least not in detail. Silica glass surfaces used in the present study and most of the other studies presented in the references were first etched in HF, and then presumably washed in water, followed by other solvents before being exposed to high temperature water or steam. With HF etching, it is likely that the initial surface of the glass was covered with Si-F groups instead of Si-OH. A remarkable characteristic of a silica surface covered by F^- ions is that the surface is hydrophobic and stable as long as the environment is dry [12]. Introduction of water into the environment converts the Si-F surface groups back to Si-OH. One might expect the conversion to occur quickly for diffusion experiments carried out in water, as in the experiments by Zouine *et al.* [2]. In a gaseous environment, the situation might be slower, so that the time for exchange of the $–F^-$ for the $–OH^-$ might take longer especially in relatively dry environments, such as used by Davis and Tomosawa [3] and Wakabayashi and Tomozawa [8]. Thus, a possible cause for the surface barrier observed for water diffusion into silica glass is coverage of the surface with F^- (or some other species), which would block the entry of water onto the silica surface. The time delay to full coverage would then be equal to the time to hydroxylate the silica surface and to obtain an equilibrium structure. Whether this is a real possibility or not remains to be tested.

MD-simulations on silica surfaces in contact with water environment have been studied so far by a number of authors, *e.g.*, Mahadevan and Garofalini [13], Milischuk and Ladanyi [14], Bourg and Steefel [15]. Concentration profiles for the water, obtained from these results, indicate that water is strongly structured by the silica surface and shows density layering up to about 0.9 nm from the silica surface, corresponding to 3 statistical monolayers [15], in which the molecular water content decreases continuously. The MD calculations seem to show a slow penetration of the silica surface with gradual buildup of SiOH on the surface. The problem with accepting this result as an explanation for the present study is that the time scale over which everything occurs is so short. A total time of 100 nm is much shorter than the real experimental times (hours) that the surface experiences in the course of a diffusion study. A fully saturated water covered surface might have developed in that time frame of a molecular dynamics study, 100 ns. As the time sequences in most molecular dynamics studies are very short, less than 100 ns, additional studies over longer times will have to be carried out to be convincing that the molecular water decrease in the first layers reflects a barrier to the diffusion process.

5 Summary

In this report, we have been able to show that the available data in the literature can be fitted to a set of equations that are consistent with the existence of a barrier to diffusion at the silica surface. The barrier could be a consequence of the replacement of the hydrophilic ≡SiOH groups that normally cover silica glass that has been exposed to water, with hydrophobic groups such as ≡SiF. Coverage of silica glass by hydrophobic groups normally prevents the wetting of silica glass by water. The kinetics of the diffusion process would then be influenced by the time required for the surface of the glass to be hydroxylated. Once hydroxylated, the surface of the glass would be in equilibrium with the water in the environment and the concentration at the surface would be fully saturated. Clearly, additional experimentation will be needed to evaluate the structure of the glass surface in order to determine if it affords sufficient resistance to water attachment to the glass surface to account for experimental observation made during diffusion studies.

Appendix: Thin test specimens

Some references [3, 5, 8] report diffusion data collected on silica glass specimens that were not thick relative to the diffusion penetration distance. In these cases it is important to have access to equations that quantify the difference between *thin specimens* and thick specimens, *i.e.,* infinite half-spaces.

For *thin specimen* of widths $2W$, the concentration as a function of time reads according to [7]

$$C(z,t) = C_0\left(1-\sum_{n=1}^{\infty}\frac{2Wh'\cos[\alpha_n(z/W-1)]\sec(\alpha_n)}{Wh'(Wh'+1)+\alpha_n^2}\exp\left[-\alpha_n^2\frac{D}{W^2}t\right]\right)\ ,\quad h'=h/D \qquad \text{(A1)}$$

with the time-dependent surface concentration

$$C(0,\,t) = C_0\left(1-\sum_{n=1}^{\infty}\frac{2Wh'}{Wh'(Wh'+1)+\alpha_n^2}\exp\left[-\alpha_n^2\frac{D}{W^2}t\right]\right) \qquad \text{(A2)}$$

where C_0 is again the saturation value, and α_n, n=1, 2, ... are the positive roots of

$$\alpha\tan\alpha = Wh' = Wh/D \qquad \text{(A3)}$$

The water profiles according to eq. (A1) are shown in Fig. A1. Figure A1a shows the profiles for fixed Biot number B=1 as a function of normalized time τ and Fig. A1b for fixed “time” τ=1 and increasing Biot numbers B. Figure A1c finally illustrates the increase of surface concentration with increasing time and heat transfer.

The water uptake per surface unit is given by

$$m(t) = m_0\left(1-\sum_{n=1}^{\infty}\frac{2(Wh')^2}{\alpha_n^2[Wh'(Wh'+1)+\alpha_n^2]}\exp\left[-\alpha_n^2\frac{D}{W^2}t\right]\right) \qquad \text{(A4)}$$

where m_0 stands for saturation value.

In the case of diffusion zones which are comparable to specimen dimensions it is favourable to introduce dimensionless quantities. Similar to thermal applications we can introduce the Biot number B as

$$B = \frac{Wh}{D} \qquad \text{(A5)}$$

and the normalised time τ as

$$\tau = \frac{D}{W^2}t \qquad \text{(A6)}$$

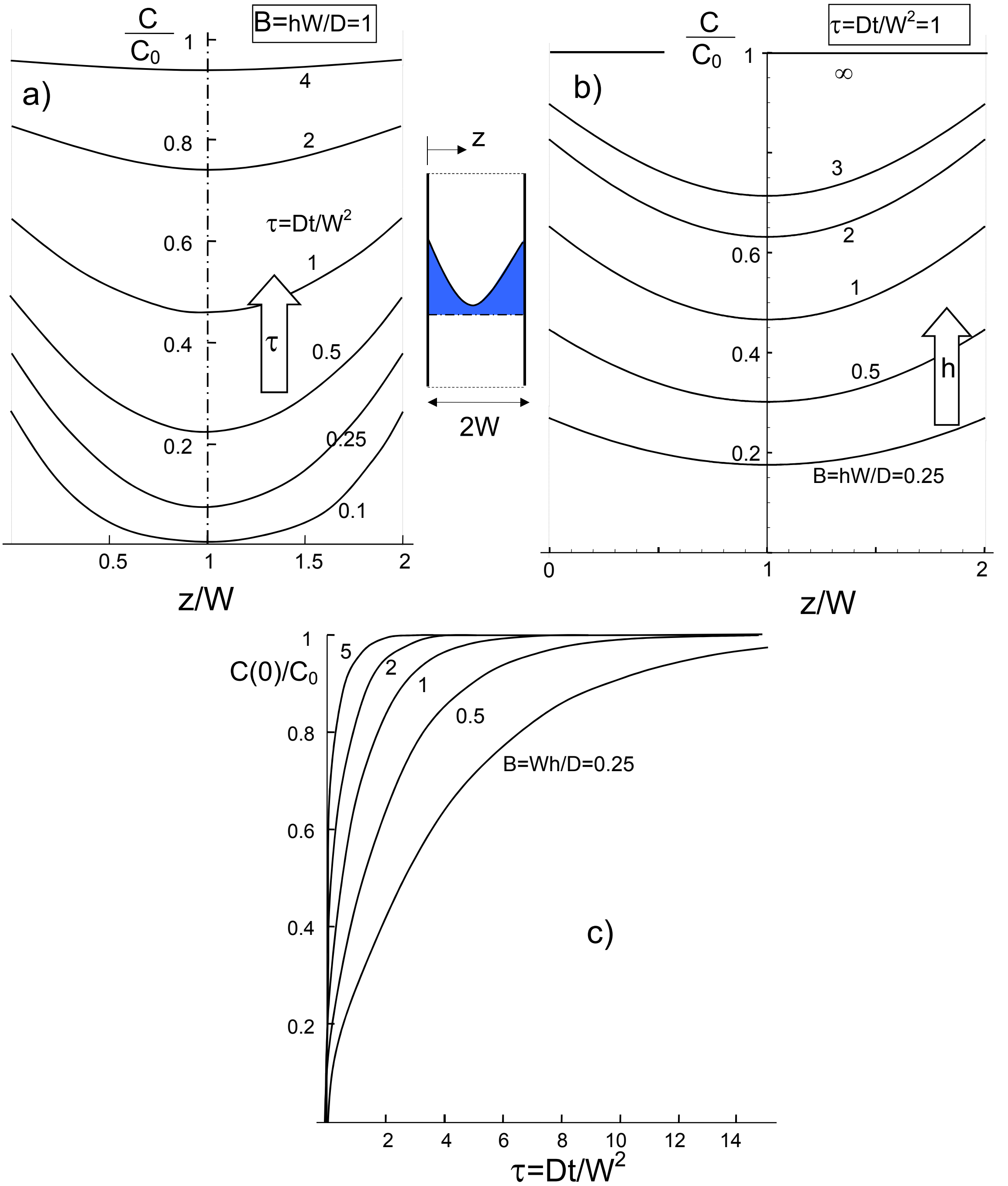

Fig. A1 a) Concentration profiles for $B=hW/D=1$ vs. time according to Eqs. A1, A1*, b) concentration profiles for fixed time $\tau=tD/W^2=1$ vs. Biot-number, c) surface concentration vs. time.

In the notation using Biot numbers, the Eqs. A1-A3 read

$$C(z,t) = C_0\left(1-\sum_{n=1}^{\infty}\frac{2B\cos[\alpha_n(z/W-1)]\sec(\alpha_n)}{B(B+1)+\alpha_n^2}\exp\left[-\alpha_n^2\,\tau\right]\right) \qquad \text{(A1*)}$$

$$C(0,\,t) = C_0\left(1-\sum_{n=1}^{\infty}\frac{2B}{B(B+1)+\alpha_n^2}\exp\left[-\alpha_n^2\tau\right]\right) \qquad \text{(A2*)}$$

$$\alpha \tan \alpha = B \tag{A3*}$$

$$m(t) = m_0 \left(1 - \sum_{n=1}^{\infty} \frac{2B^2}{\alpha_n^2 [B(B+1) + \alpha_n^2]} \exp\left[-\alpha_n^2 \tau \right] \right) \tag{A4*}$$

It should be emphasized that here only a renaming was made in order to allow a direct comparison with thermal results.

For ideal mass transfer, $B \rightarrow \infty$, the zeroes of Eq. A3* are simply given by

$$\alpha_n = (2n-1)\frac{\pi}{2} \tag{A7}$$

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