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A reason for the occurrence of mass-transfer coefficients at silica surfaces

Günter Schell, Claudia Bucharsky, Susanne Wagner, Theo Fett

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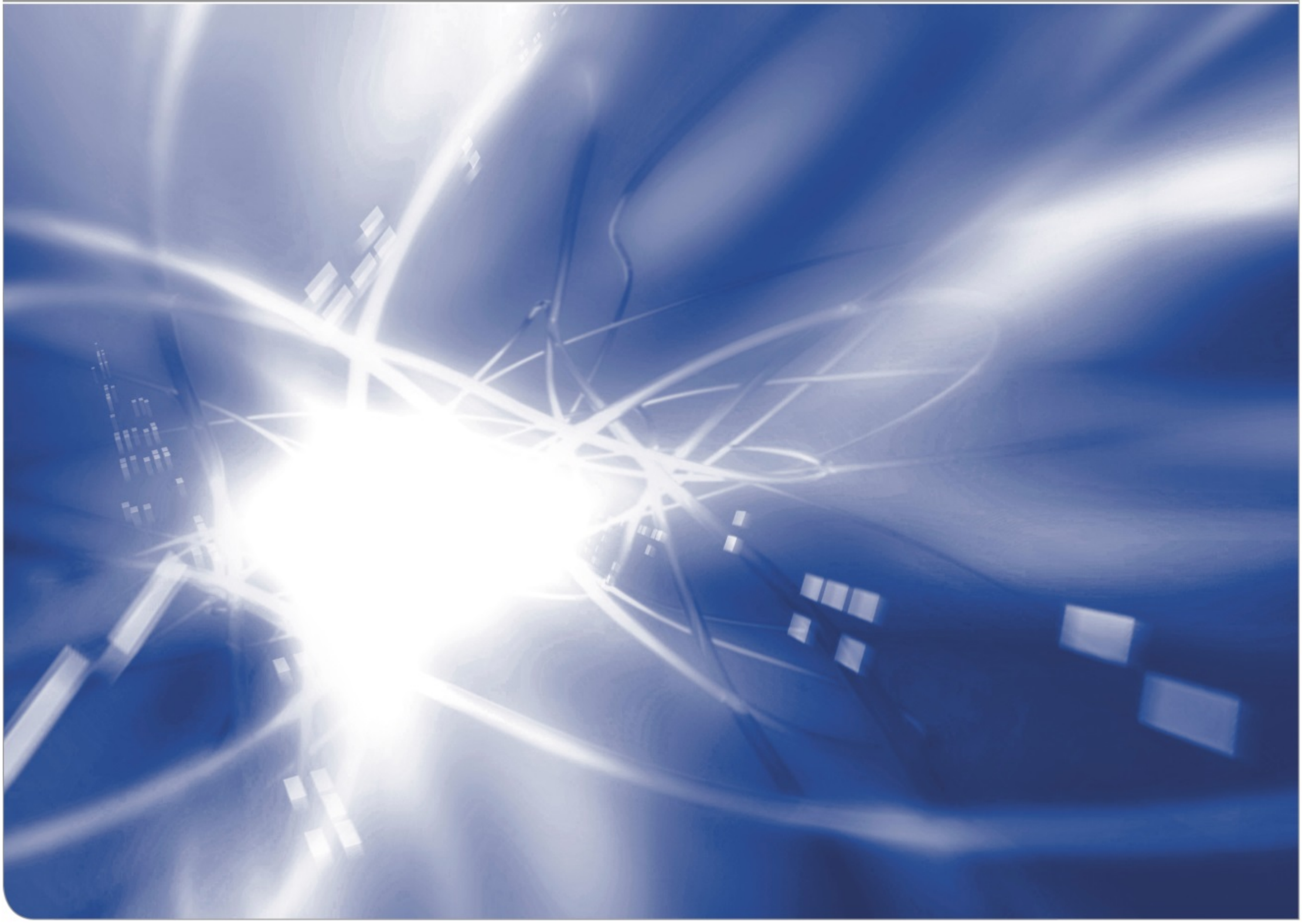

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Abstract

At silica surface exposed to a water vapour environment, there is a monotonously increasing water concentration observed that calls for a limited mass transfer from the humid environment to the surface. Such behaviour is characterized by a “mass transfer coefficient". We have demonstrated in several studies that silica glass surfaces may present a barrier to the diffusion of water into silica. We could interpret the experimental diffusion results of Oehler and Tomozawa (2004) and those of Helmich and Rauch (1993). Such a surface layer formed by diffusion and water reaction with the surface material, was studied by Mahadevan and Garofalini (2008).

Compressive hydrostatic stresses in the surface layers reach a maximum value of $\sigma_{sw,h} = -2.8\,\text{GPa}$. Due to such high compressive stresses, the water diffusivity must be strongly reduced within this thin layer and, consequently, also the mass transfer coefficient. These effects will be considered in detail in this report.

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1 Introduction

It was shown early in the literature that the behavior of silica in water is not in all cases determined by the surface concentration C=C_0=const. In Fig. 1a, measurements of the surface concentration of water in silica are shown as a function of the residence time in a saturated water vapor atmosphere. The results of Fig. 1b obtained with the NRA method indicate a steadily increasing water concentration.

In the experimental results of Fig. 1a by Oehler and Tomozawa [1] for $C(z=0,t)$ is a clear contradiction of the very often used assumption of a constant surface value for the water concentration. Consequently, one cannot assume that the surface concentration of water, $S(z=0)$ or $C(z=0)$, stays constant under the conditions used for the experiment. Nevertheless, the condition

$$C(z=0,t)\equiv C(0)=C_0=\text{constant} \tag{1}$$

is very often used as a boundary condition for solving the diffusion equation. For a semi-infinite body, this assumption would result in the solution

$$C=C_0\operatorname{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) \tag{2}$$

which is well established for liquid water as the environment [2]. Figure 1b represents the surface water concentration as measured by Helmich and Rauch [3] that also illustrates the time-dependent increase of the water concentration at the surface.

There is, however, 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

$$\frac{dC}{dz}=\frac{h}{D}(C-C_0)\quad \text{at }\ z{=}0, \tag{3}$$

where again C_0 is the concentration of molecular water reached at z=0 for $t\rightarrow\infty$ and D is the water diffusivity in the glass. Following the suggestion by Doremus (Section 4.7 in [4]), the phenomenological parameter h in (3) may be interpreted as a *reaction parameter* for a slow surface reaction that limits the entrance of molecular water species. The parameter h is also called a *mass transfer coefficient* for diffusion.

The definition of the mass transfer coefficient by equation (3) reflects the analogy to the heat transfer coefficient and allows a direct application of the solutions of the heat conduction equations to the diffusion problem.

The equivalent formulation of eq.(3), as used by Doremus [4], reads

$$D\frac{dC}{dz}=Dh'(C-C_0)\quad \text{at }\ z{=}0, \tag{4}$$

and defines the coefficient simply by

$$h' = \frac{h}{D} \tag{5}$$

with units of reciprocal distance, [*h*']=1/m. We prefer the formulation of the surface boundary condition by eq.(3), which is analogous to thermal shock, but we also report results in terms of *h*'. Of course, each of the two notations leads to the same system of mathematical equations.

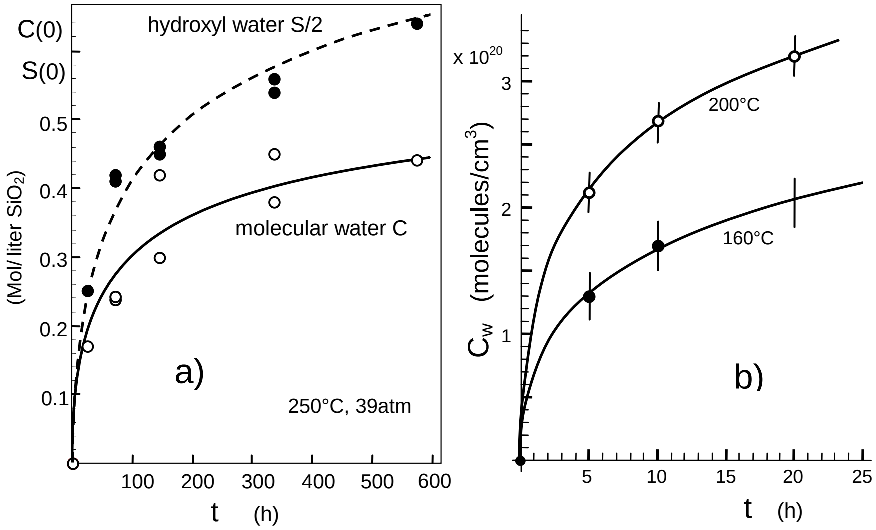

Fig. 1 a) Molecular water (*C*) and hydroxyl water content (*S*/2) at the surface of silica for 250°C at an equilibrium vapour pressure of 39atm from [1], b) Solubility of water at silica surfaces under saturation pressure by Helmich and Rauch [3], water molecules per cm^3 vs. soaking time *t*.

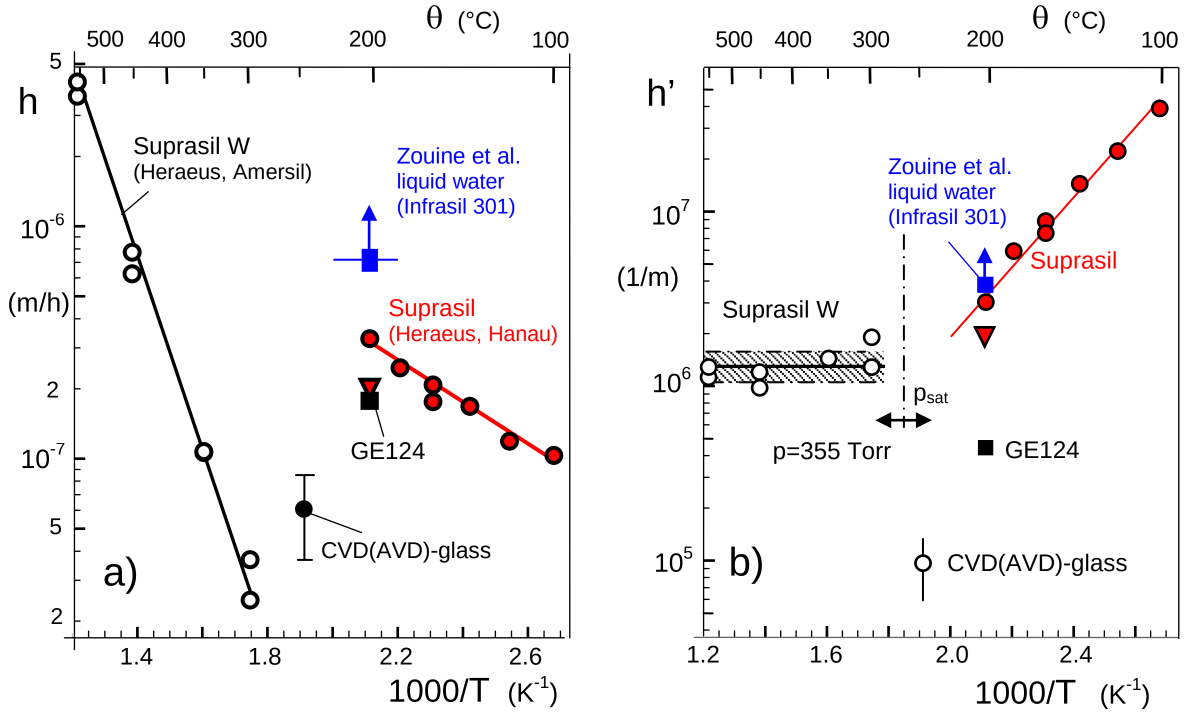

Fig. 2 a) Mass-transfer parameter *h* as a function of temperature; b) mass transfer coefficient in the form of *h*'=*h*/*D*.

2 Mass transfer coefficients

2.1 A possible reason for a limited water entrance

A simpler phenomenological description is possible by assuming that at the silica surface a barrier exists to the transport of water across the surface of the glass. Such a barrier gives rise to a *mass transfer coefficient* for diffusion, which slows the passage of water into the glass. In this way, we can duplicate the experimental diffusion results of Oehler and Tomozawa [1] and those of Helmich and Rauch [3]. A diffusion barrier is clearly observed when silica is exposed to water vapour but seems to be less pronounced in liquid water, as results by Zouine et al. [5] show. Immersion in liquid water differs significantly from immersion in the vapour, because silica dissolves in the liquid [6,7,8], but not in the vapour [6]. Hence, in liquid water, the surface is constantly being regenerated and any barrier that might form is dissolved away.

2.2 Diffusion barrier due to a hydroxyl surface layer

In [9] a model was suggested in which a strongly reduced diffusivity in an extremely thin surface layer of <1nm thickness is caused by high compressive swelling stresses because of a very high hydroxyl concentration in this layer (for a physical description of such a barrier see [9], Section 1.3).

Such layers at silica surfaces are well known from literature. Already in Iler's handbook on silica (Table 6.1 in [10]) many results for the hydroxyl surface concentration are compiled showing data in the range of 4.0-10.0 OH/nm^2. After including newer results by Zhuravlev [11], 4.6/nm^2, Mahadevan and Garofalini [12], 3.8/nm^2, and Banerjee et al. [13], 5.2/nm^2, an average value of 6.6/nm^2 and a standard deviation of 2.1/nm^2 may be concluded.

Investigations of silica surfaces showed that silica is more reactive chemically at the surface than in the bulk. In contrast to the SiO_2-structure in the bulk of silica, undercoordinated Si and O atoms occur at the free surface because of missing neighboured atoms. These are more reactive so that when this surface is exposed to water vapour, water molecules react nearly instantaneously with the SiO_2 surface molecules to form SiOH as has been shown by molecular dynamic computations (see e.g. Mahadevan and Garofalini [12]).

The depth extension of the surface layer is very small. On the basis of molecular dynamic (MD) computations, Mahadevan and Garofalini [12] obtained the concentration distributions in the surface layer as shown in Fig. 5. Whereas the hydroxyl concentration extends over a range of 0.7nm, the main part occurs within about 0.3nm in the centre of the layer. Banerjee et al. report the high concentration disappearing with distance from the surface with a steep gradient of about 0.2-0.3nm.

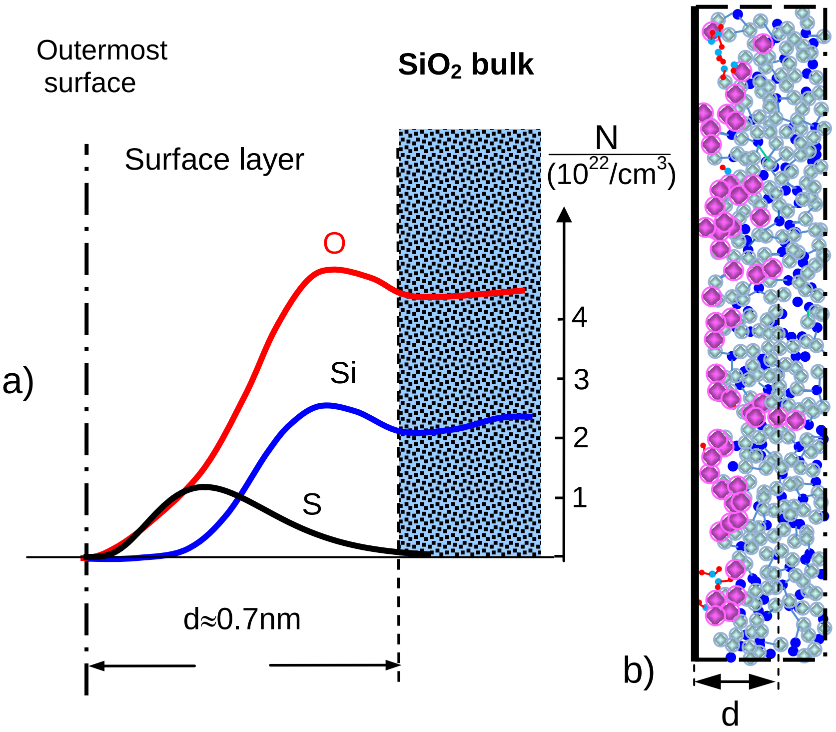

Fig. 3 a) At a free silica surface water reacts nearly instantaneously with under-coordinated silica species in a thin surface layer of about 0.7 nm thickness; per 2-coord O (and 3-coord Si) 1 H_2O molecule reacts to SiOH (curves according to Mahadevan and Garofalini [12]), b) surface layer on silica (pink: H, grey: O, blue: Si).

Water molecules are trapped at the "free" ends of the surface molecules for a short while resulting in a dynamic equilibrium: water molecule coming in from the environment are then captured by the surface, while water released from the surface is free to diffuse deeper into the bulk as has been studied by computer modelling of the diffusion process [14,15,16].

2.3 Swelling stresses in the surface layer

The reaction between water and silica shows a volume swelling as was reported by Shelby [17]. Therefore, the effect of the water-silica reaction is the generation of *swelling strains*. *Swelling stresses* are a consequence of the mechanical boundary conditions. A volume element in a thick plate that undergoes swelling cannot freely expand. If the diffusion zone is small compared to the component dimensions; expansion is completely prevented in the plane of the surface and can only take place normal to the surface plane.

At a free surface, the stress state is plane stress and, consequently, also stresses caused by swelling are equi-biaxial (σ_x=0)

$$\sigma_y = \sigma_x = -\frac{\varepsilon_v E}{3(1-\nu)} = -\frac{E}{3(1-\nu)}\kappa S \tag{6}$$

where E=72 GPa is Young's modulus and ν=0.17 is Poisson's ratio.

With these parameters, the swelling stresses read simply

$$\begin{aligned} &\sigma_y = \sigma_x = -28\,\mathrm{GPa}\times S \\ \Rightarrow\quad &\sigma_{sw,h} = \tfrac{1}{3}(\sigma_x + \sigma_y) = -18.6\,\mathrm{GPa}\times S \end{aligned} \tag{7}$$

with S in weight-%. Due to such high compressive stresses, the water diffusivity must be strongly reduced within this thin layer.

When swelling stresses are present, the diffusivity is given by the following equation [18]:

$$D = D_0 \exp\left[\sigma_{sw,h}\,\frac{\Delta V_w}{RT}\right] \tag{8}$$

with the diffusivity D_0 of the bulk material and the effective volume ΔV_w generally in the order of the molar volume of water [18]. Measurements of the effective volume for glass by Lezzi et al. [19] resulted in $\Delta V_\mathrm{w} \cong 16\pm 2$ cm^3/mol. R is the gas constant and T the absolute temperature.

The composition of a silica surface after contact with water molecules is illustrated in Fig. 3a. It is conceivable that such a layer can show a completely different diffusion behavior than the bulk material. Such a difference would be necessary to form a diffusion barrier. When the silica surface is exposed to a water vapour environment, additional water molecules are docked at the hydroxyl groups.

The type of dependency can easily be expressed by an equation that satisfies the conditions of disappearing hydroxyl concentrations at the outermost surface, $S(0)=0$, and far away in the bulk material, $S(\infty)\to 0$.

$$S = a\,z^n \exp[-b\,z] \tag{9}$$

The maximum S-concentration, S_max, is reached at $z_\mathrm{max}=n/b$:

$$S_\mathrm{max} = \frac{a}{e^n}\left(\frac{n}{b}\right)^n \tag{10}$$

and the total S-concentration per surface unit

$$m_S = \int_0^\infty S\,dz = \frac{a}{b^{1+n}}\Gamma(1+n) \tag{11}$$

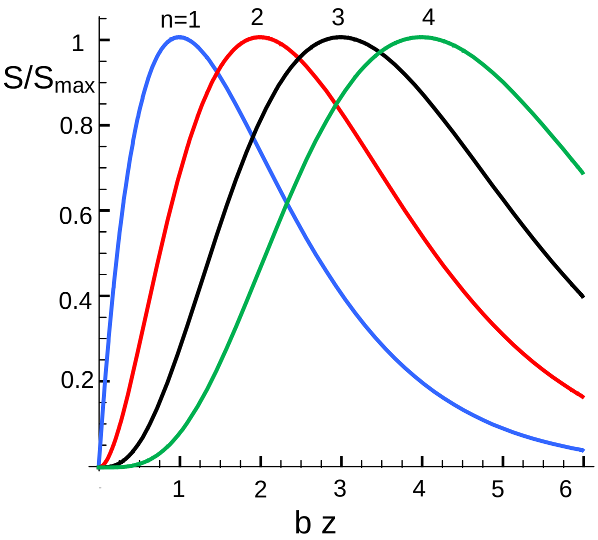

Fig. 4 Shape of distributions according to eq.(9) for different exponents *n*.

A comparison of the curve types is given in Fig. 4 for different values of *n*. These curves show that the best agreement of curve shape with the result in Fig. 3a seems to appear for $2<n<4$. Figure 5a shows the fitting curves for *n*= 3, 3.5, and 4 for 6 data points (circles) extracted from the curve for *S* in Fig. 3a. A least-squares regression analysis, illustrated by the curves in Fig. 5b, yields a "best" parameter set of $n=7/2$, $a=2.45\ 10^{22}/\mathrm{cm}^3$, $b=1.579$ Å^{-1}. In this case, the location of the maximum *S*-concentration is at $z_{\max}\cong 2.22$ Å with

$$S_{\max} \cong 1.20\times10^{22}\,/\,\mathrm{cm}^3 \qquad (12)$$

$$m_S \cong 3.7\ \mathrm{SiOH\,/nm}^2$$

In Table 1 the results from a curve-fitting evaluation near $n=7/2$ are compiled as a function of *n*.

n	$z_{\max}$ (Å)	$S_{\max}$ ($10^{22}/\mathrm{cm}^3$)	m_S ($1/\mathrm{nm}^2$)
5/2	2.15	1.16	4.10
3	2.18	1.16	3.77
7/2	2.22	1.20	3.66
4	2.24	1.23	3.54

Table 1 Parameters for eq.(9) obtained from Figs. 3 and 5

The quantity S in terms of the hydroxyl mass concentration is

$$S(\mathrm{wt}-\%) = \frac{S(\mathrm{molecules/cm}^3)}{N_L}\frac{M_S}{\rho} \qquad (13)$$

and represented by the right ordinate in Fig. 5a. The mole mass for hydroxyl water is $M_S=17$ g/mol, $N_L=6.022\times10^{23}$ molecules/mol, and the density $\rho=2.2$ g/cm^3.

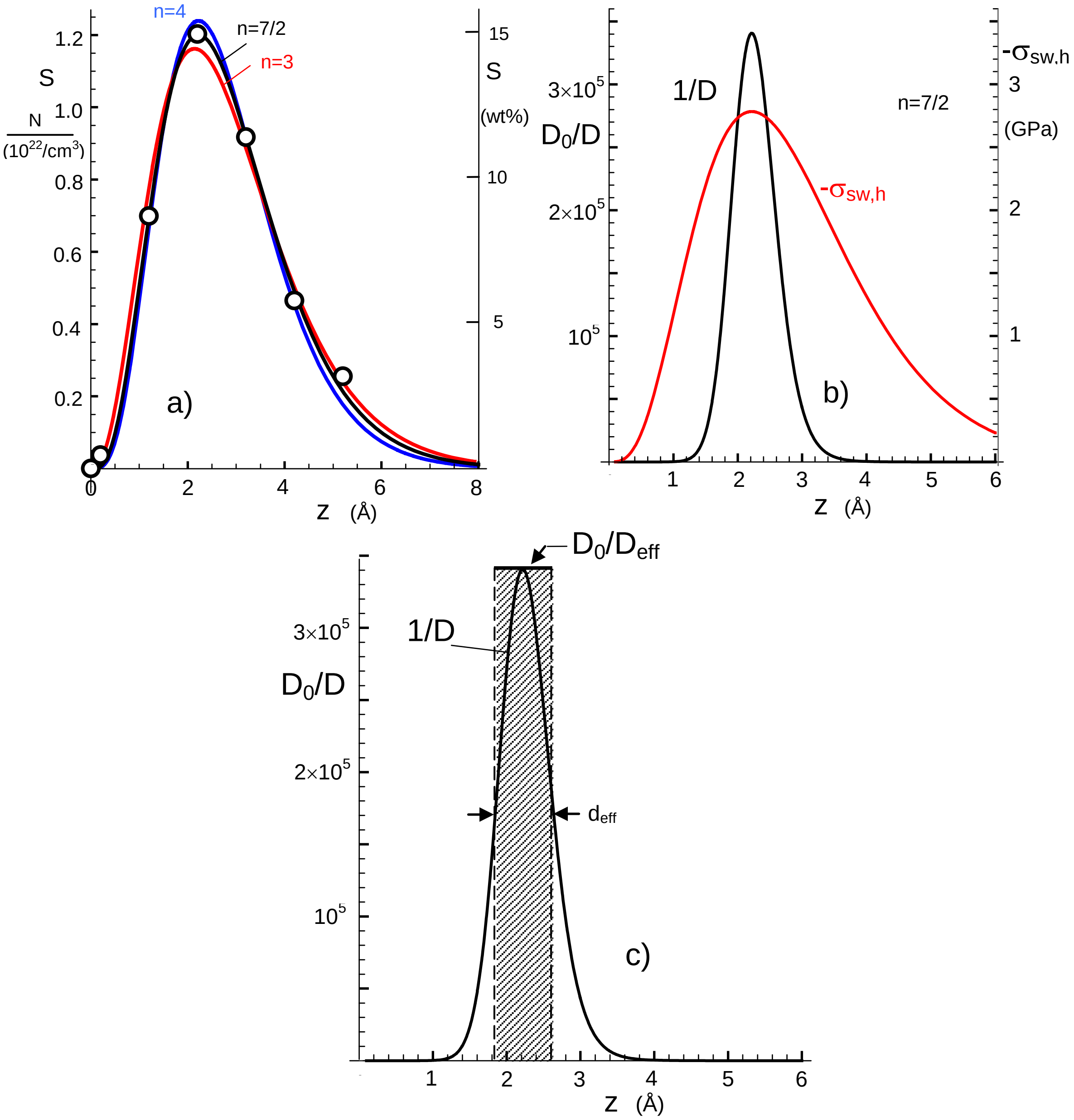

Fig. 5 a) Data for the application of a least-squares fitting procedure (circles) and two results (curves), b) diffusivity and swelling stresses for *n*=7/2 at 200°C, c) replacing the distribution of the diffusivity by a constant effective diffusivity D_{eff} over the effective width d_{eff}.

3 Comparison of measurements with predictions by swelling stresses

A surface layer formed by diffusion and water reaction with the surface material, Fig. 3, was studied by Mahadevan and Garofalini [12]. In Fig. 5a, the hydroxyl concentration is given in weight percent (right ordinate). Unfortunately, the swelling behaviour of the under-coordinated Si and O atoms of silica is not known. We tentatively apply the dependency of volume swelling strain as a function of hydroxyl concentration, $\varepsilon_v(S)$, as an approximation. The hydrostatic swelling stresses can then be computed as shown in [9]. Figure 5b represents the result.

The reciprocal of the diffusivity stands for a diffusion resistance of the surface layer. Compressive hydrostatic stress reaches a maximum value of $\sigma_{sw,h} = -2.8\,\mathrm{GPa}$.
Due to such high compressive stresses, the water diffusivity must be strongly reduced within this thin layer. When swelling stresses are present, the diffusivity is given by equation (8).

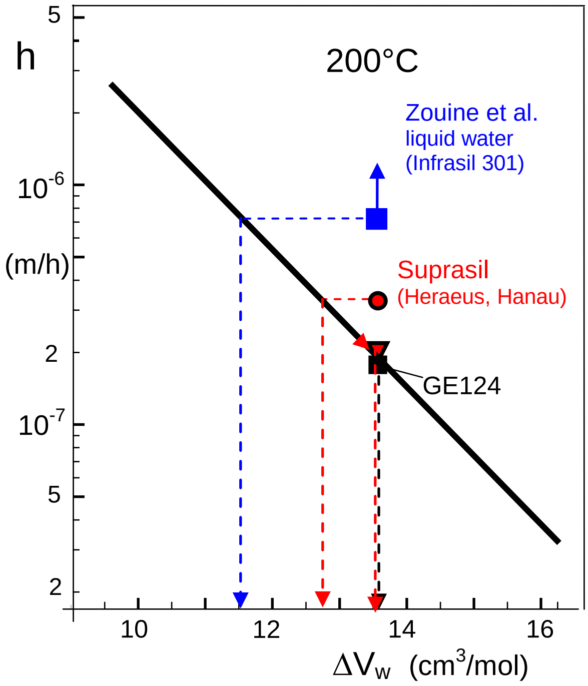

Fig. 6 Mass transfer coefficient computed by eqs.(15) and (16), compared with measured data from Fig. 2b on Infrasil 301 and Suprasil.

According to the derivation in Sections 1.9 and 12.8 of Carslaw-Jaeger [20], the mass-transfer (or heat transfer) coefficient is related to the constant diffusivities $D<D_0$ in the thin surface layer, d, under swelling stresses by

$$h = \frac{D}{d} \quad \text{at} \;\; z=0, \tag{14}$$

In the case of a varying swelling stress, $\sigma_{sw,h}(z)$, the diffusivity in the surface layer must also vary as can be seen from eq.(8) and Fig. 4. Since eq.(14) needs constant diffusivity over the zone thickness d, we replace the distribution in Fig. 5b by a rectangular of constant effective diffusivity D_{eff}. Due to the small rectangle width d_{eff}, we can write in good approximation

$$h \cong \frac{D_{eff}}{d_{eff}} \quad \text{at} \;\; z=0, \tag{15}$$

with the parameters D_{eff} and d_{eff} defined via

$$\frac{d_{eff}}{D_{eff}} = \int_0^\infty \frac{dz}{D(z)}, \quad D_{eff} = D_{\min} \tag{16}$$

Based on the fitting curve in Fig. 5b and 5c for a temperature of 200°C, eq.(16) resulted for $\Delta V_w = 16$ cm^3/mol in: d_{eff}=0.862 Å, $(D_0/D)_{\max}$= 341000.
Next, we calculated the mass transfer coefficient for 200 °C according to eq.(15) and compared it with the measurements for the same temperature where most results are available (see Fig. 2a). Figure 6 shows the prediction according to equations (15) and (16) for the scatter range of the activation volume delta ΔV_w, with $\Delta V_w = 13$, 14, 15, 16, and 17 cm^3/mol. The calculations lead to the horizontal black bars in Fig. 6. The best agreement between measurement and prediction would be: $\Delta V_w = 13$ cm^3/mol.
The value of 13 cm^3/mol seems somewhat too low compared to that of Lezzi et al. of 16 cm^3/mol.

Some causes for the deviations from $\Delta V_w = 16$ cm^3/mol can be identified:

- The swelling behaviour of under-coordinated bonds is not yet known and could therefore not be included in the predictions.
- SiO_2-rings are damaged by the hydroxyl generation. This leads to a significant decrease of the Young's modulus in tension [9, 21]. Nevertheless, also in compression a reduction of several percent is expected.

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