Karlsruhe Institute of Technology

# Mass-transfer coefficient for water at silica surfaces

## - Effect of surface dissolution?

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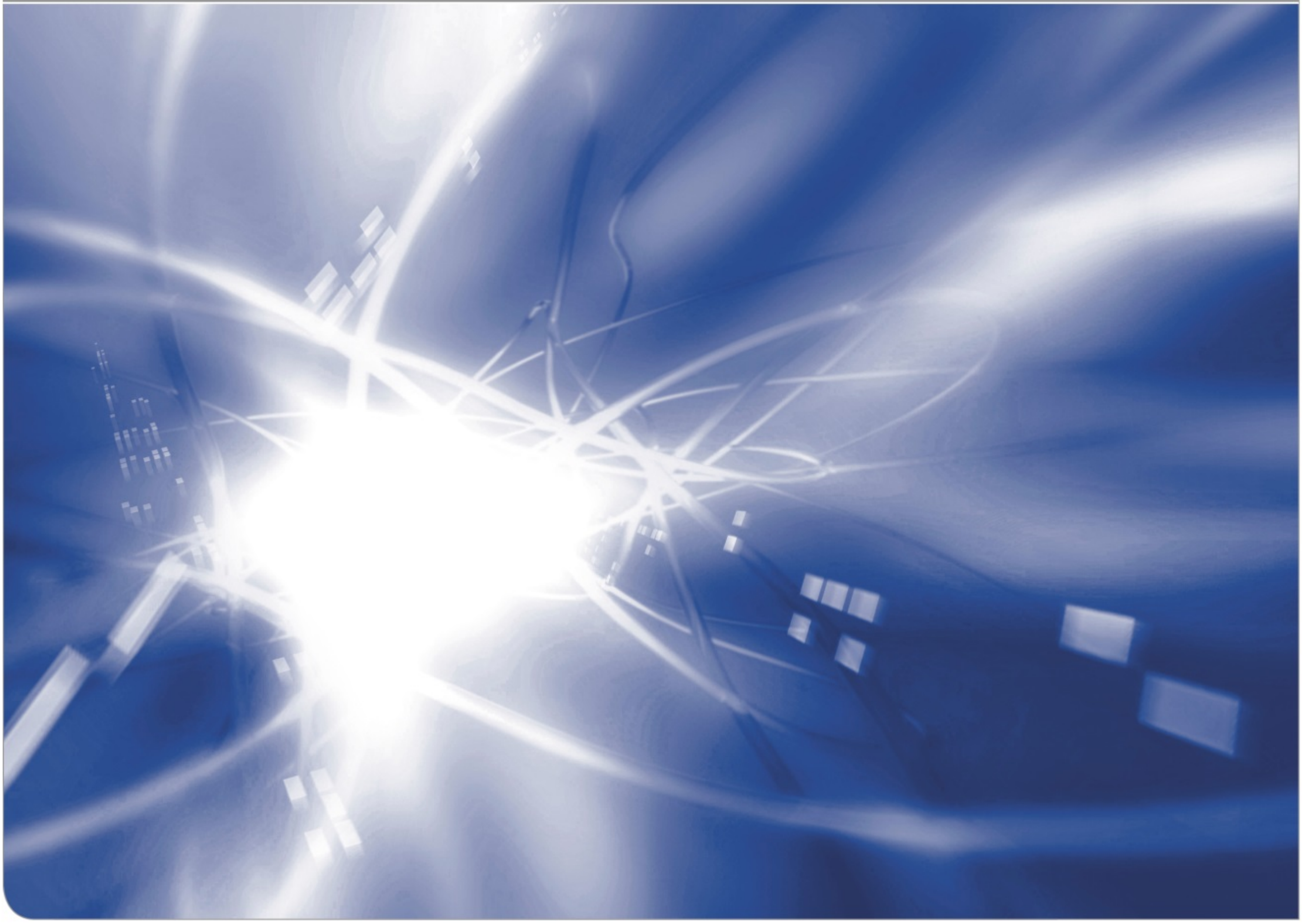

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# Abstract

In earlier evaluations of literature results, it was found that the mass transfer when storing silica in liquid water was significantly greater than in tests in a steam atmosphere under saturation vapor pressure.

In the literature, different glass qualities were compared and it is conceivable that small material differences may lead to the observed results. On the other hand, it can be shown qualitatively that there is also the possibility of mass removal through dissolution, which is different for liquid water and saturated steam.

This is the subject to be addressed in this report.

# Contents

# 1 Introduction

Water penetrated into silica reacts with the silica network according to

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

with the concentration of the hydroxyl $S = [\equiv\text{SiOH}]$ and that of the molecular water $C = [H_2O]$. The equilibrium constant of this reaction is at temperatures of $\theta<450°C$

$$k = \frac{S}{C} \tag{2}$$

Water concentration measurements were carried out on silica by Helmich and Rauch in [1] using the technique of Nuclear Reaction Analysis [1]. The silica specimens were soaked in saturated water vapour at 200°C, 15.3 bar (1.53MPa). Figure 1a shows the surface concentrations of the water from H-measurements. From data fitting and using $S_0/C_0$=2.1 it results as shown in [2]:

$$S_0 = 2.1\times C_0 = 3.42\times 10^{20}\,/\text{cm}^3,\ C_{w,0} = 2.05\ C_0 = 3.51\times 10^{20}\,/\text{cm}^3. \tag{3}$$

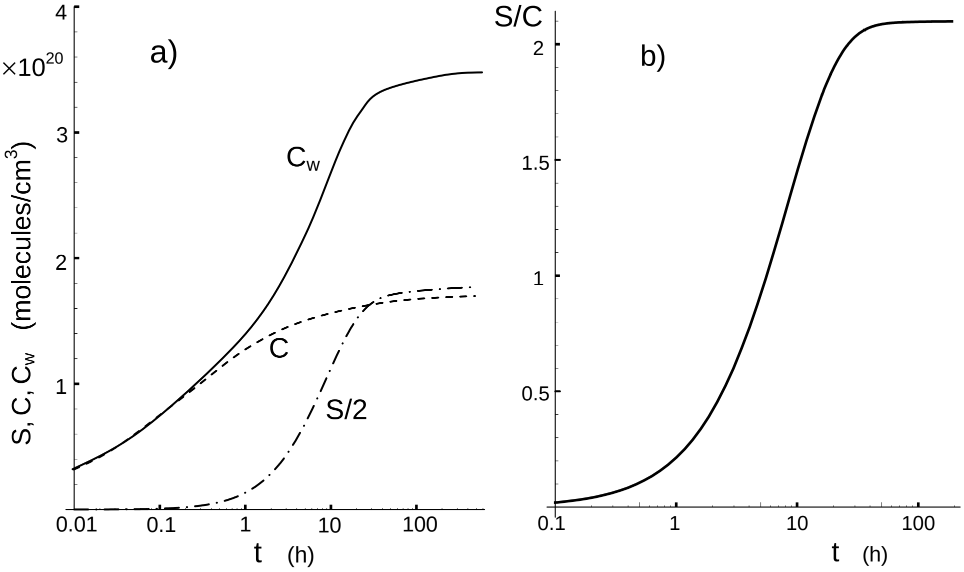

**Fig. 1** a) Total water concentration $C_w$ at the surface at a temperature of 200°C in saturated water vapour by Helmich and Rauch [1], Dashed curves: hydroxyl and molecular water concentrations, b) $S/C$-ratio vs. time.

Since only six data points were available for the fitting analysis, and four parameters had to be determined, the results do not have high accuracy. Hence, confidence intervals were not determined. The two water species, $C$ and $S/2$ are shown in Fig. 1a. Finally, the time-dependent *S*/*C*-ratio is represented in Fig. 1b. From this diagram, we can expect that *S*/*C* equilibrium is reached after about 30 h.

# 2 Diffusion at silica surfaces

## 2.1 Problem of moving border by limited mass transfer

Water profiles in silica surfaces are mostly described by

$$C_w = C_w(0)\ \mathrm{erfc}\left(\frac{z}{2b}\right) \tag{4}$$

where the diffusion length *b* is defined by

$$b = \sqrt{Dt} \tag{5}$$

(see Fig. 2a). The present report is intended to evaluate more complicated water profiles. Water concentrations at silica surfaces under saturation pressure are available from an investigation by Zouine et al. [3].

In our report SWP 214 [4], we had considered a special case for the dissolution of glass surfaces by water, as it was early treated by Danckwerts [5]. We implicitly dealt with the case that the glass/water reaction does not lead to a change of state. The surface of the solid is continuously saturated with the dissolved substance. An example of this is the dissolution of a solid into a supernatant liquid or the absorption of a solid or liquid into another. In any case, the glass is presumed to be destroyed by a process, which depends solely on and is proportional to the concentration of water in the glass.

In a first example, treated early by Danckwerts [5] it is assumed that the ideal diffusion law resulting from the water profile (4) applies to the diffusion of unreacted dissolved substances through the medium. The lower the solubility of the dissolved substance, the higher the probability that these conditions are met. Under the conditions of the chemical reaction between water and glass, the profile of the water in the glass results from the derivation of Danckwerts [5]. When $C$=$C(z)$ is the concentration of solute at a distance $z$ below the surface and $C(0)$ is the concentration at the surface ($z$ = 0), $t$ is time, and $k$ is the rate constant of the reaction between dissolved water and glass, the diffusion differential equation was solved in [5] with the result of

$$\frac{C}{C(0)} = \tfrac{1}{2}\exp[-z\sqrt{k/D}]\times \mathrm{erfc}[z/2b-\sqrt{kt}] + \tfrac{1}{2}\exp[z\sqrt{k/D}]\times \mathrm{erfc}[z/2b+\sqrt{kt}] \tag{6}$$

As shown by Carslaw and Jaeger (Section 2.7 in [9]), the concentration profile under mass-transfer conditions, $C(z)$ resulting for the boundary condition of a semi-infinite body is given by

$$C(z,\,t)/C_0 = \mathrm{erfc}\left[\frac{z}{2\sqrt{Dt}}\right] - \exp\left[\frac{h}{D}z + \frac{h^2}{D}t\right]\mathrm{erfc}\left[\frac{z}{2\sqrt{Dt}} + h\sqrt{\frac{t}{D}}\right] \tag{7}$$

where $h$ is the mass transfer coefficient and $C_0$ the saturation concentration ($t \to \infty$).

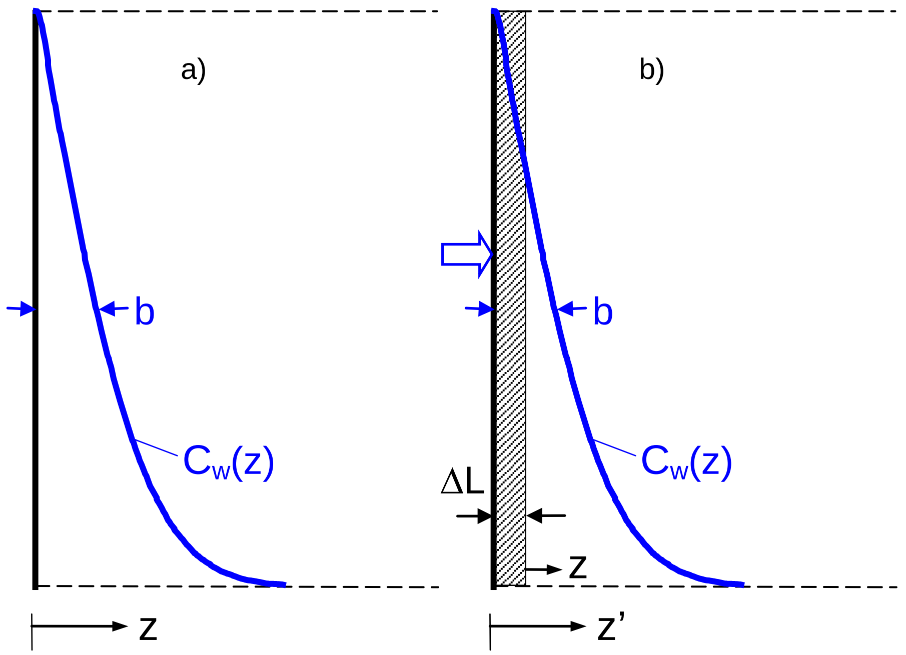

**Fig. 2** a) Simultaneous diffusion and chemical reaction, b) material removal on the surface by dissolving the glass in liquid water.

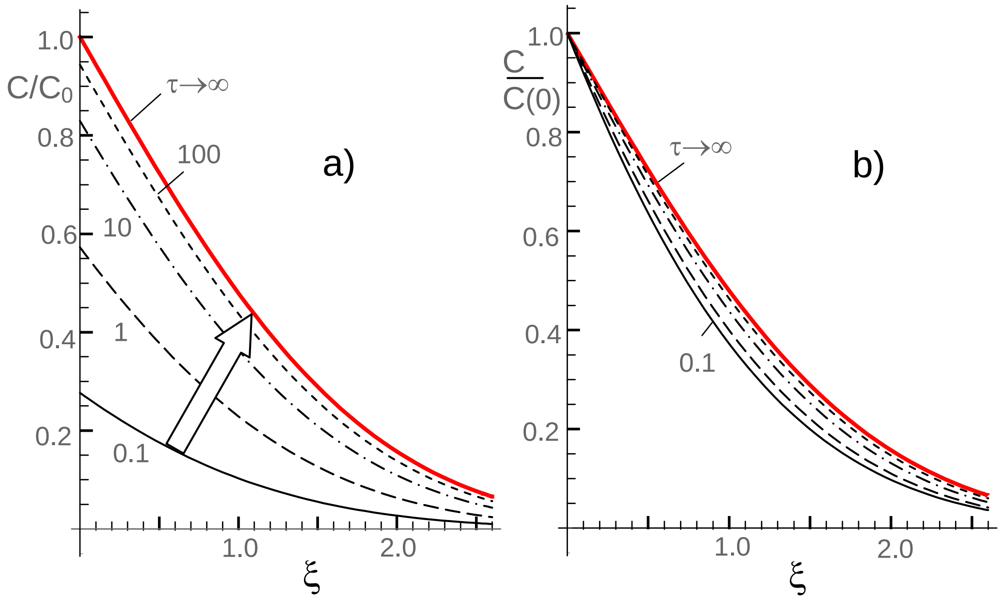

**Fig. 3** a) Diffusion profiles at different normalized times $\tau$ for glass affected by mass transfer, b) concentrations, normalized on their surface values $C(0)=C(\xi=0)$.

For a description of the behavior of real silica materials, one needs the concentration at the surface $z\rightarrow 0$, $C(0)$, the dissolution rate $D_{\mathrm{dis}}$ (or $v$) and the diffusion constant $D$. These parameters are shown in Fig. 4a and Fig. 4b.

For reasons of simplicity we introduce a normalized dimensionless time $\tau$ and normalized depth coordinate $\zeta$, defined by

$$\tau = \frac{h^2}{D} t \,;\; \zeta = \frac{z}{\sqrt{Dt}} \tag{8}$$

Then, eq.(6) reads rewritten

$$\underbrace{\frac{C(\zeta,\tau)}{C_0} = \mathrm{erfc}\left[\frac{\zeta}{2}\right]}_{regular\ part} - \exp[\zeta\sqrt{\tau} + \tau]\mathrm{erfc}\left[\frac{\zeta}{2} + \sqrt{\tau}\right] \tag{7a}$$

Equation (6) is plotted in Fig. 3a, and in Fig. 3b for the ordinate normalized on the actual surface concentrations.

## 2.2 Dissolution effect for liquid-water soaking

Another reason for a deviation in the water distribution in the surface diffusion zone is caused by the dissolution of the surface material in water and a simultaneous surface removal. As the glass dissolves in water, the glass/water-interface moves in the direction of diffusion. This must result in a deviation of the water concentration profile from the pure erfc law, eq.(4), which was derived for a fixed glass surface.

Dissolution rates $D_{\mathrm{dis}}$ are plotted in Fig. 4a. The circles correspond to a soda-lime glass that should have the same dissolution behavior as silica [6]. The square shows the rate for silica at 150°C in a 0.0167 M $CaCl_2$ solution by Dove et al. [7]. Table 1 compiles experimental data.

| Temperature | $t$ (h) | $C_0$ ($10^{20}$ H/cm$^3$) | $v$=$D_{\mathrm{dis}}$ (m/s) | $D$ (m$^2$/s) |
|---|---|---|---|---|
| 60°C | 1416 | 1.9 | $3\times10^{-14}$ | $2.9\times10^{-20}$ |
| | 2136 | 1.8 | | $3.4\times10^{-20}$ |
| 100°C | 336 | 2.8 | $8\times10^{-13}$ | $2.9\times10^{-19}$ |
| | 1319 | 2.6 | | $3.7\times10^{-19}$ |
| 140°C | 253 | 3.8 | $1\times10^{-11}$ | $5.8\times10^{-18}$ |
| | 1147 | 3.8 | | $1\times10^{-17}$ |
| 200°C | 22 | 6.9 | $1.5\times10^{-10}$ | $7.7\times10^{-17}$ |
| | 45 | 7.3 | | $8.5\times10^{-17}$ |
| | 92.5 | 6.3 | | $6.0\times10^{-17}$ |

**Table 1** Results from experimental data reported by Zouine et al. [3].

In our opinion, the strange soaking behavior is caused by the interaction of diffusion with dissolution of the surface material. The dissolution of the glass in water on the surface and the simultaneous diffusion of water into the glass lead to a diffusion problem with a moving diffusion source showing a correspondingly high mathematical effort, as can be seen, for example, from the work by Danckwerts [5], Masters [8], Carslaw and Jeager [9] (Section 11), Crank [10] (Section 13), and Babich [11].

Dissolving of glass in water results in a removed silica layer of thickness $\Delta L$ at the surface (Fig. 2b).

The surface reaction in water vapour, for example, can be regarded as an example of the whereabouts of the reaction products. The vapor phase is hardly capable of transporting away the generated $H_4SiO_4$ and the surface coverage with water is limited to only a few layers of water molecules, for which saturation should be reached very quickly. The conditions are completely different when liquid water is used as the surrounding medium. In this case, the resulting $H_4SiO_4$ molecules can be easily transported away.

If during the reaction the state can change, the analysis was early performed by Stefan [12] with the steady solution (after a transient running-in phase)

$$C = C(0)\exp\left[-\frac{v}{D}z\right] \tag{9}$$

where the origin is on the actual surface, $z = 0$, and $v$ is the dissolution rate of the boundary moving in $z$-direction. The consequence of the glass dissolution on the surface is therefore a reduction in the current diffusion layer. The effective diffusion layer thickness, i.e. the half-value thickness $z_{1/2}$ for the concentration $C/C(0) = 1/2$ is simply given by

$$z_{1/2} = \frac{D}{v}\ln[2] \tag{10}$$

and decreases with increasing dissolution rate. The equivalent thermal problem is a melting surface with continuously removal of melted material, e.g. by blowing away. Equations (4) and (9, 10) give rise for the definition of an effective time $t_{\mathrm{eff}}$ via

$$b_{eff} = \tfrac{1}{2} z_{1/2} \Rightarrow t_{eff} = \frac{D}{4v^2}\ln^2[2] \cong 0.12\frac{D}{v^2} \tag{11}$$

For a description of the behavior of real silica materials, one needs the maximum concentration at the surface $z \to 0$, $C_0$, the dissolution rate $D_{\mathrm{dis}}(=v)$ and the diffusion constant $D$. These parameters are shown in Fig. 4a and Fig. 4b. For 200°C we find:

$$v = D_{dis} = 1.5\times 10^{-10}\ \mathrm{m/s},\ D = 7\times 10^{-17}\ \mathrm{m^2/s} \tag{12}$$

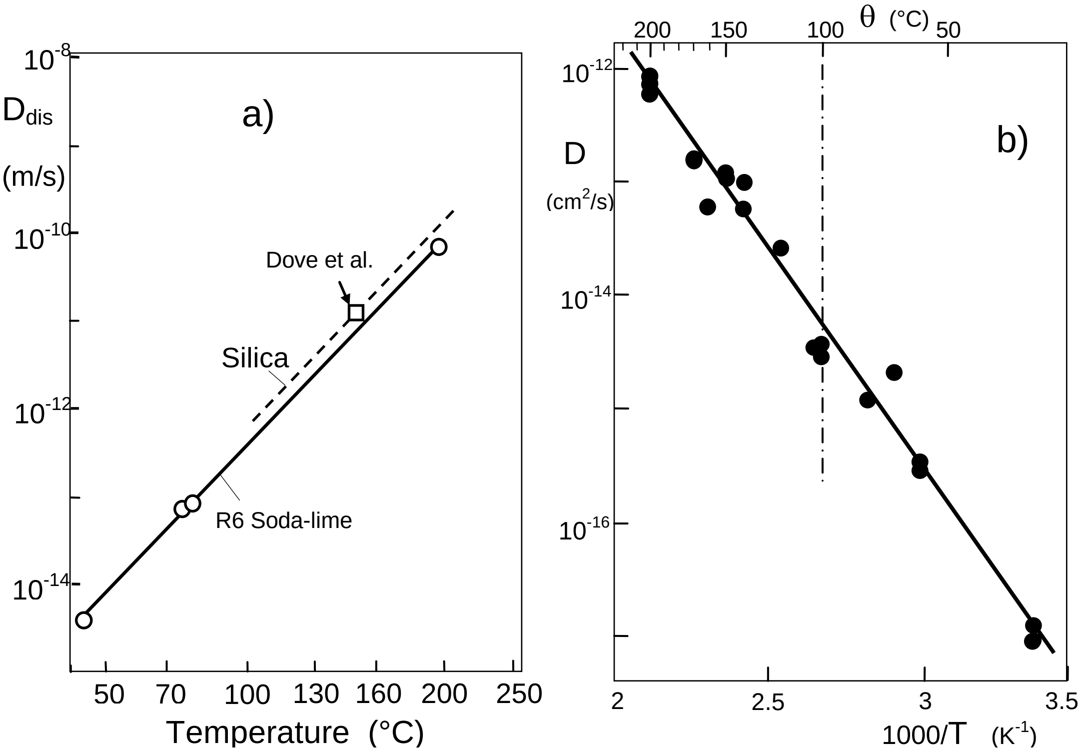

**Fig. 4** a) Rate for dissolution of silica in water (circles: data for soda-lime glass R6 with about equal dissolution behaviour as silica, reported by Perera and Doremus [6], square: result from Dove et al. [7]), b) material removal on the surface by dissolving the glass in liquid water.

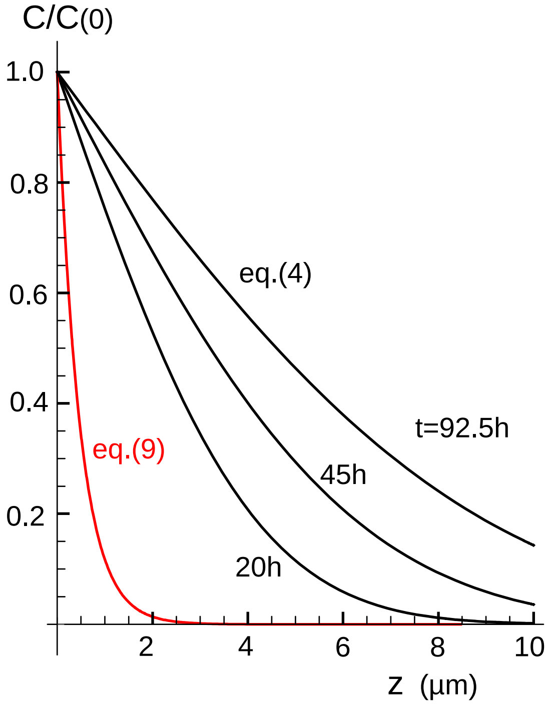

**Fig. 5** Water profiles in silica at 200°C: In the absence of liquid water (black curves), in liquid water showing dissolution (red curve)

### 2.3 Dissolution effect on mass-transfer coefficient

In order to understand the behaviour of glass-water surfaces at least qualitatively, two boundary cases should be considered here. In the liquid-water tests, the glass dissolution should be present on the surface (Case I). In the tests in water vapour, there is not any material removal at the surface (Case II).

I) In soaking tests in liquid water, fresh glass surfaces are practically always available due to the continuous dissolution of the material and the possible removal from the surface. The consequence is a negligibly thin water penetration zone.

II) In the tests in water vapour, no material removal can take place on the surface due to the lack of a liquid phase. The water in the thin multilayers is very early saturated.

With the parameters (12), the concentration curves to be expected according to eq.(4) for the 3 measurement periods in [3] were calculated. The results are represented in Fig. 5a by the black curves. The red curve shows the time-independent solution according to Stefan [12], eq.(9).

It should be noted that the stationary layer thickness of the water profile in silica might be considerably lower under the possibility of surface dissolution in liquid water than in the case of samples in water vapour. The mass transfer is affected by the stress state at the surface and must read

$$h = A\exp\left[\frac{Q_h + \sigma_h \Delta V}{RT}\right] = h_0 \exp\left[\frac{\sigma_h \Delta V}{RT}\right] \tag{13}$$

where $h_0$ stands for the mass transfer coefficient in the absence of stresses and $\Delta V>0$ is an activation volume. This volume must be positive since the ring structure at the surface is widened by tension and compacted by compressive stresses as occur under swelling. The hydrostatic swelling stress is

$$\sigma_h = -\frac{2\,\varepsilon_v\,E}{9(1-\nu)} \tag{14}$$

[2], where $E$ is Young's modulus, $\nu$ is Poisson's ratio, and $\varepsilon_v$ the volume swelling strain as determined in [13]: $\varepsilon_v=0.97\,S$, ($S$ = hydroxyl mass concentration).

Finally, Fig. 6 shows the comparison of the results for mass transfer coefficients obtained in water vapour (red symbols) and from liquid water tests (blue symbol). The black arrow illustrates the differences of results for the tests at 200°C. The transfer coefficients are for the liquid water by a factor of at least 3 larger than those of water vapour. This result is in agreement with the expectation from eq.(13).

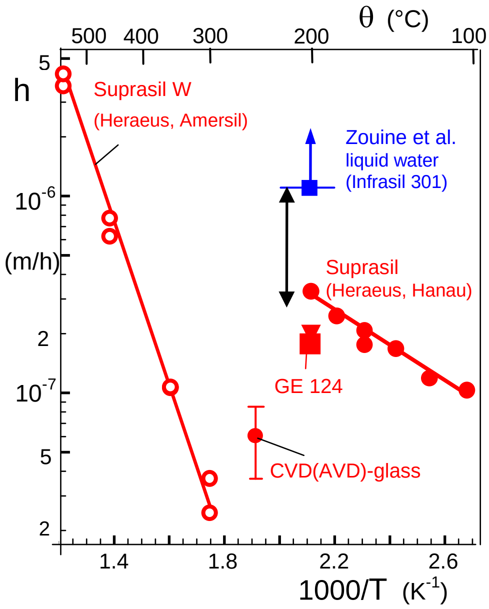

**Fig. 6** Mass-transfer parameter *h* as a function of temperature, from [14]. Red symbols: Tests in water vapour, Blue: Test in liquid water. Black arrow indicates the different behaviour at 200°C in water vapour and liquid water showing a factor of about $h_{\mathrm{liquid}}/h_{\mathrm{vapour}} \geq 3$.

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