Mass Transfer of Water at Silica Surfaces

- Extension of the data base to lower temperatures

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Abstract

In two previous reports we have dealt with the description of the time dependence of the water content at the surface of silicate glass by mass transfer (SWP 73 and SWP 94). Literature measurements in the range of 200°C<T<550°C were now evaluated and described by mass transfer coefficients. In the present report, this range is extended to temperatures >100°C. Measurements by Helmich&Rauch serve as a basis.

A step change in the mass transfer coefficient is found at 200°C.

Contents

1 Basic results

1.1 Mass transfer coefficient

At a silica surface exposed to a water vapour environment, there is a monotonously increasing water concentration C observed [1], that can be described by a diffusion surface condition of

$$\frac{dC}{dz} = \frac{h}{D}(C - C_0) \quad \text{at} \quad z{=}0, \tag{1}$$

where D is the water diffusivity, $C_{w,0}$ the asymptotically reached water concentration and a parameter h that describes reduced water entrance [2, 3]. Under this boundary condition the concentration at the surface reads as a function of time t [4]

$$C_w(0, t)/C_{w,0} = 1 - \exp\left[\frac{h^2}{D}t\right]\text{erfc}\left[h\sqrt{\frac{t}{D}}\right], \tag{2}$$

Equation (2) allows the determination of the parameter $h/\sqrt{D}$ from measurements of the time-dependent surface water concentration. This is also possible by evaluating swelling stresses at the surface, which are proportional to the hydroxyl water concentration, $\sigma_{sw} \propto S \propto C_w$. This has been outlined in detail in [5]. For this purpose, one has to solve

$$1 - \exp\left[\frac{h^2}{D}t\right]\text{erfc}\left[h\sqrt{\frac{t}{D}}\right] = \frac{C_w}{C_{sat}} = \frac{S}{S_{sat}} = \frac{\sigma_{sw}}{\sigma_{sat}} \tag{3}$$

with experimentally obtained right-hand sides. The saturation values of concentrations and stresses are C_{sat}, S_{sat}, and σ_{sat}. The solutions of eq.(3) were determined in [6] by application of the Mathematica Routine *FindRoot* [7].

1.2 Previous results

Results from [3, 5, 6] are introduced in Fig. 1. The results are based on water-uptake measurements in 355 Torr water vapour by Wakabayashi and Tomozawa [8] (triangles and circles), by surface water concentration measurements under water saturation pressure by Oehler and Tomozawa [1] (solid circle), and curvature measurements on vapour-soaked silica disks heat-treated under saturation pressure at about $\theta{=}200°C$ by Wiederhorn et al. [9] (open squares).

The straight-line behaviour of the parameter $h/\sqrt{D}$ for $\theta{>}200°C$ was determined in [3] and could be represented by

$$\frac{h}{\sqrt{D}} = A \exp\left(-\frac{Q}{RT}\right) \tag{4}$$
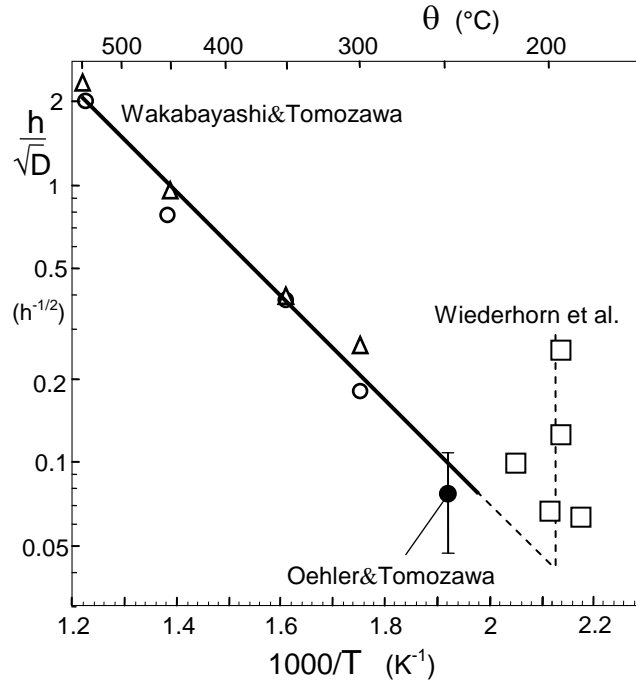
with $A \cong 330$ ($1/h^{1/2}$) and $Q = 35.1$ (kJ/mol).

Fig. 1 Parameter $h/\sqrt{D}$ as a function of temperature from [3,5,6].

2. Results for the low-temperature region $\theta \leq 200°C$

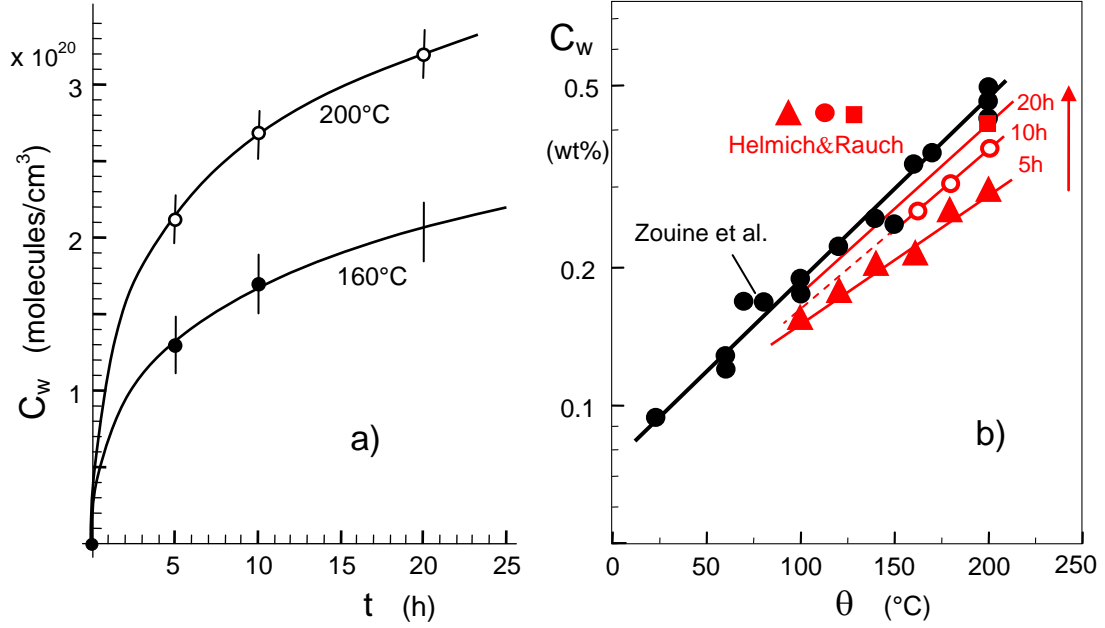### 2.1 Water concentration measurements by Helmich and Rauch

Figure 2 compiles data of the surface water concentration as a function of time (Fig. 2a) by Helmich and Rauch [12] and of temperature (Fig. 2b) by Helmich and Rauch (red symbols) and Zouine et al. [10] (black circles). Whereas the measurements by Helmich and Rauch were performed on specimens heat-treated in water vapour under saturation pressure, the results by Zouine et al. [10] were found on liquid-water soaked specimens. In both cases nuclear reaction analysis was employed.

The results of Fig. 2a for $\theta=200°C$ represent oxygen concentrations showing only small scatter, the data for $\theta=160°C$ were derived from hydrogen measurements exhibiting rather large scatter as is indicated by the scatter bars. The parameters $h/\sqrt{D}$ were computed via eq.(2). The straight line through the measurements by Zouine et al. [10], Fig. 2b, can approximately be described by the simple expression [11]

$$C_w = 0.000780 \exp(0.00868\,\theta) \quad \text{for } 23°C \leq \theta \leq 200°C \tag{5}$$

with the temperature θ in °C.

Fig. 2 Solubility of water at silica surfaces under saturation pressure, a) Surface water concentration by Helmich and Rauch [12], water molecules per cm³ vs. soaking time *t*, b) concentration vs. soaking temperature θ by Zouine et al. [10] (black circles) and Helmich and Rauch [12] (red symbols).

Vapour treatment	C_w [12] (wt-%)	$h/\sqrt{D}$ (1/√h)
200°C/5h	0.288	0.955
200°C/10h	0.367	0.998
180°C/5h	0.265	1.222
180°C/10h	0.316	1.143
160°C/5h	0.217	1.131
160°C/10h	0.272	1.332
140°C/5h	0.200	1.539
120°C/5h	0.17	1.586
100°C/5h	0.15	1.955

Table 1: Water concentration at silica surfaces under saturation pressure and heat-treatment times of 5h and 10h based on measurements by Helmich and Rauch [12].

2.2 Full temperature region from 100°C to 550°C

Figure 3 shows the results of Fig. 1 once more together with the data of Table 1 obtained from the measurements of Helmich and Rauch [12]. These new data are introduced as the red squares. It has to be noted that the data in Fig. 3 were obtained on different silica qualities. The material investigated by Wakabayashi and Tomozawa [8] was Suprasil W (Heraeus-Amersil), Helmich and Rauch [12] used also Suprasil (Heraeus, Hanau). The tests by Wiederhorn et al. [9] were carried out on GE 124. Oehler and Tomozawa [1] tested a high-purity silica glass produced via CVD.

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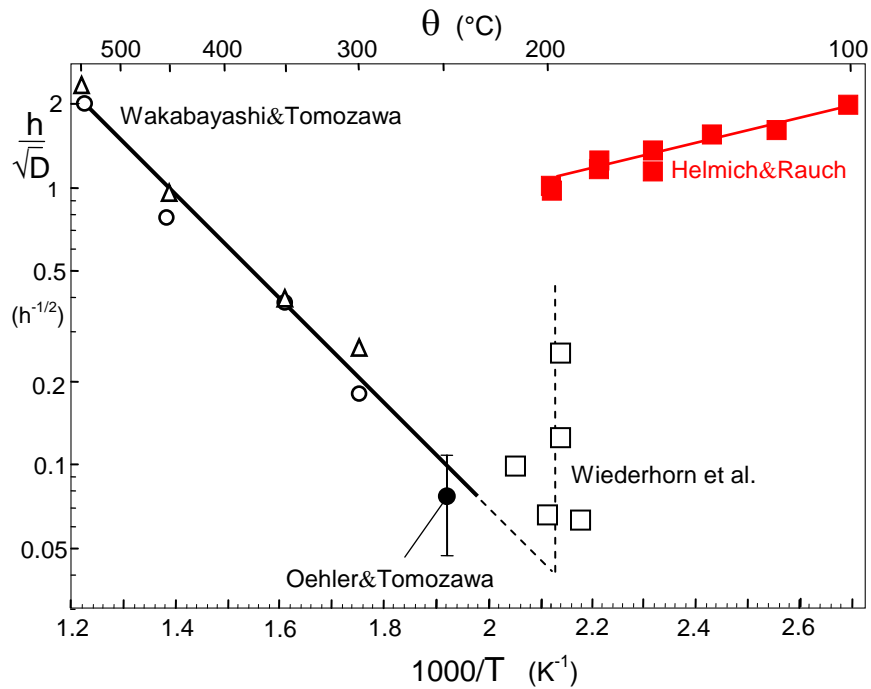
Fig. 3 Parameter $h/\sqrt{D}$ from Fig. 1. Additionally plotted red squares: Data obtained from measurements by Helmich and Rauch [12].

Final Remark

There remain two interesting points for future considerations:

- At about $\theta=200°C$ the mass transport from the vapour into silica is very complicated. At the moment, the reason for the strongly different behavior at this temperature is not yet sufficiently understood. An attempt should be made to clarify whether the somewhat curious temperature dependence in Fig. 3 could be due to the different materials.

- In addition to the trivial fact that the individual investigations in [1, 9, 12] deal with different glass qualities, the abrupt change in $h/\sqrt{D}$ might be interpreted on the description of the water covering at SiO_2 surfaces proposed by Zhuravlev [13].

References

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