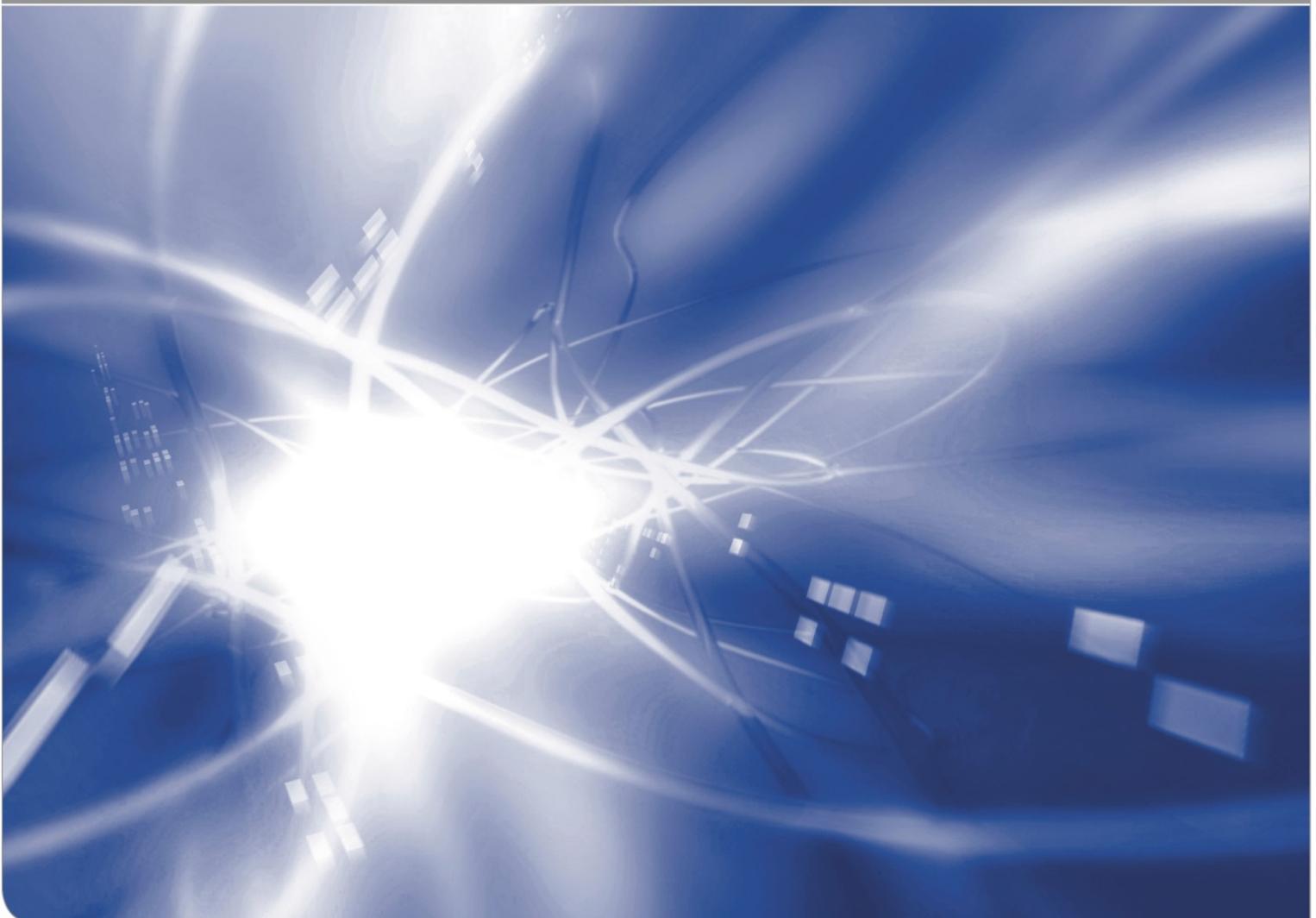


Mass transfer coefficient for silica in liquid water at 200°C

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KIT SCIENTIFIC WORKING PAPERS 206



Institute for Applied Materials

Impressum

Karlsruher Institut für Technologie (KIT)
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2022

ISSN: 2194-1629

Abstract

In previous reports on the mass transfer coefficient of quartz glass in water, we were able to determine that this is significantly larger in liquid water than in saturated water vapor as the surrounding medium.

From literature results by Zouine et al. (2007) a lower limit value of the time parameter h/\sqrt{D} in eq.(4) of $>10^{-6} \text{ h}^{-1/2}$, could be deduced for 200°C and liquid water. One explanation for this result could be, among other things, an increased roughness due to the dissolution of the surface layers of the glass in water than is to be expected for water vapour.

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1 Surface concentration for tests in liquid water

In previous publications [1-8] we used experimental measurements of the water concentration on silica surfaces from the literature and described their time dependence with respect to the mass transfer from the liquid phase to the glass. Here, the transition from saturated steam was considered. The present report considers the behavior of glass in liquid water.

Water concentrations in liquid water are reported by Zouine et al. [9]. At some temperatures, these authors measured water content at the surface after different times. The results are shown in Fig. 1 by the squares. Based on the measurements by [9] we can sufficiently approximate the temperature dependence of the water concentration C_w in H_2O -molecules per cm^3 :

$$C_w = A \exp(B \theta) \quad (1)$$

with $A=0.6 \times 10^{20}$ water molecules/ cm^3 and $B=0.0087/^\circ C$. This dependency is introduced in Fig. 1 as the straight line. Especially for $200^\circ C$ we obtain $C_w \approx 3.4 \times 10^{20}$ H_2O -molecules/ cm^3 .

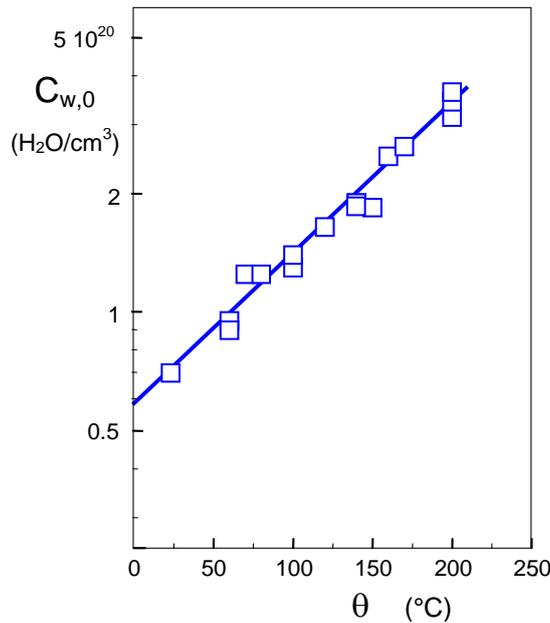


Fig. 1 Water concentration at silica surfaces (water in mass-%) from Zouine et al. [9] on Infrasil 301, (Heraeus, Hanau).

2 Estimation of a lower limit mass transfer coefficient

At a silica surface exposed to a water vapour environment, there are simultaneously increased molecular and hydroxyl water concentrations observed [10] that can be described by a diffusion surface condition of

$$\frac{dC_w}{dz} = \frac{h}{D}(C_w - C_{w0}) \text{ at } z=0, \quad (2a)$$

where D is the water diffusivity in the glass, C_{w0} the asymptotically reached water concentration and a parameter h that describes reduced water entrance [1,11]. The parameter h is called a *mass transfer coefficient* for diffusion.

The definition of the mass transfer coefficient by equation (2a) 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.(2), as used by Doremus [11], reads

$$D \frac{dC_w}{dz} = D h'(C_w - C_{w0}) \text{ at } z=0, \quad (2b)$$

and defines the coefficient simply by

$$h' = \frac{h}{D} \quad (3)$$

with units of reciprocal distance, $[h']=1/m$. The authors of this report also work intensively in the field of thermal shock behavior of brittle materials. For this reason we prefer the formulation of the surface boundary condition by eq.(2a), which is analogous to thermal shock. In the current report, however, both description options of describing the boundary condition, eqs.(2a) and (2b), should be used.

Especially, the concentration at the surface $z \rightarrow 0$ reads as a function of time t according to Carslaw and Jeager [12]

$$C_w(0, t) / C_{w0} = 1 - \exp\left[\frac{h^2}{D}t\right] \operatorname{erfc}\left[h\sqrt{\frac{t}{D}}\right], \quad (4)$$

For a water temperature of 200°C we obtain from eq.(1): $C_{w0} \approx 3.4 \times 10^{20}$ H₂O-molecules/cm³.

Figure 2a shows the surface concentrations at the surface from measurements by Helmich and Rauch [13] at 200°C as a function of square-root of time t as the red circles. A least-squares fit of these data by eq.(4) results in the best parameter set of $h/\sqrt{D} = 0.57 \text{ h}^{-1/2}$ [0.454; 0.69] and $C_{w0} \approx 3.43 \times 10^{20}$ [3.27 × 10²⁰; 3.58 × 10²⁰] H₂O-molecules/cm³, the latter in best agreement with the measurements by Zouine et al. [9] in liquid water. The numbers in brackets are the 90% Confidence Intervals CI.

The best fit is introduced in Fig. 2a by the curve. The horizontal line represents the fitted C_{w0} together with its 90% CI as the dashed lines. The blue squares indicate the surface concentrations by Zouine et al. [9] for liquid water.

Figure 2b represents the same procedure for the Zouine et al. data [9] in liquid water, with the 200°C-data again plotted as blue squares. The curves represent eq.(4) computed for $C_{w0} \approx 3.4 \times 10^{20}$ H₂O-molecules/cm³ and several parameters h/\sqrt{D} . From this fig-

ure we can conclude a lower limit value of $h/\sqrt{D} \geq 2/\sqrt{h}$ indicated by the blue bold curve.

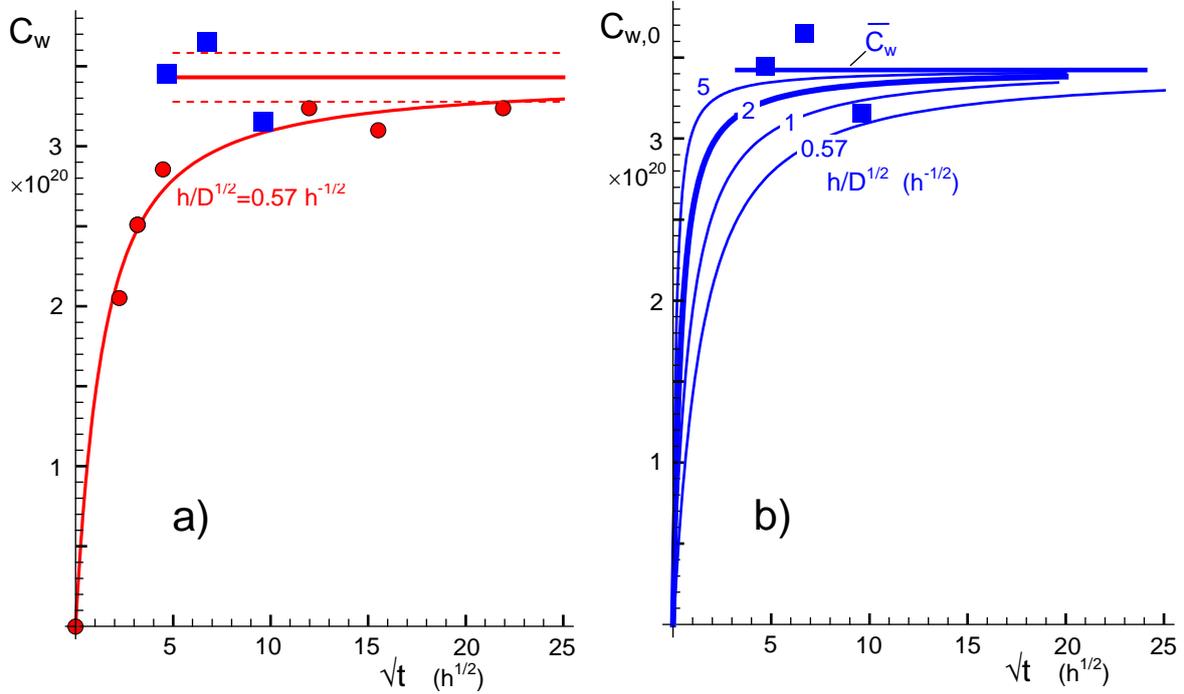


Fig. 2 Concentration of water molecules per cm^3 at 200°C , a) red data: Results from Helmich and Rauch [13], red curve: best fit according to eq.(4), blue data: Results from Zouine et al. [9]. Red straight line: asymptotic concentration C_{w0} with 90%-Confidence Intervals given by the dashed lines, b) Data from Zouine et al. [9] for 200°C together with some assumed time dependencies according to eq.(4), blue horizontal line given by eq.(1).

The results of [7] are plotted here again in Figs. 3a-3c. For a comparison of the result for liquid water from Zouine [9] with data obtained in [7], the result from Fig. 2 is introduced in Figs. 3a-3c as a blue square. In this context, it should be noted that the diffusivities vary from one material to another (see Fig. 2b in [7]). Table 1 compiles the different parameter combinations h , h/\sqrt{D} , h/D . The parameter h/\sqrt{D} seems to be the most important quantity since it governs the rate of water concentration increase at the surface.

	Data sources	$h/\sqrt{D}=h'\sqrt{D}$ ($\text{h}^{-1/2}$)	$h/D=h'$ (m^{-1})	$h=h'D$ (m/h)
liquid water	Zouine et al. [9]	≥ 2.0	$\geq 3.7 \times 10^6$	$\geq 1.07 \times 10^{-6}$
saturated vapour	Helmich and Rauch [13]	1.0	3.04×10^6	3.3×10^{-7}
saturated vapour	Wiederhorn et al. [14]	0.28	4.1×10^5	1.9×10^{-7}

Table 1 Compilation of mass transfer coefficients in different representations.

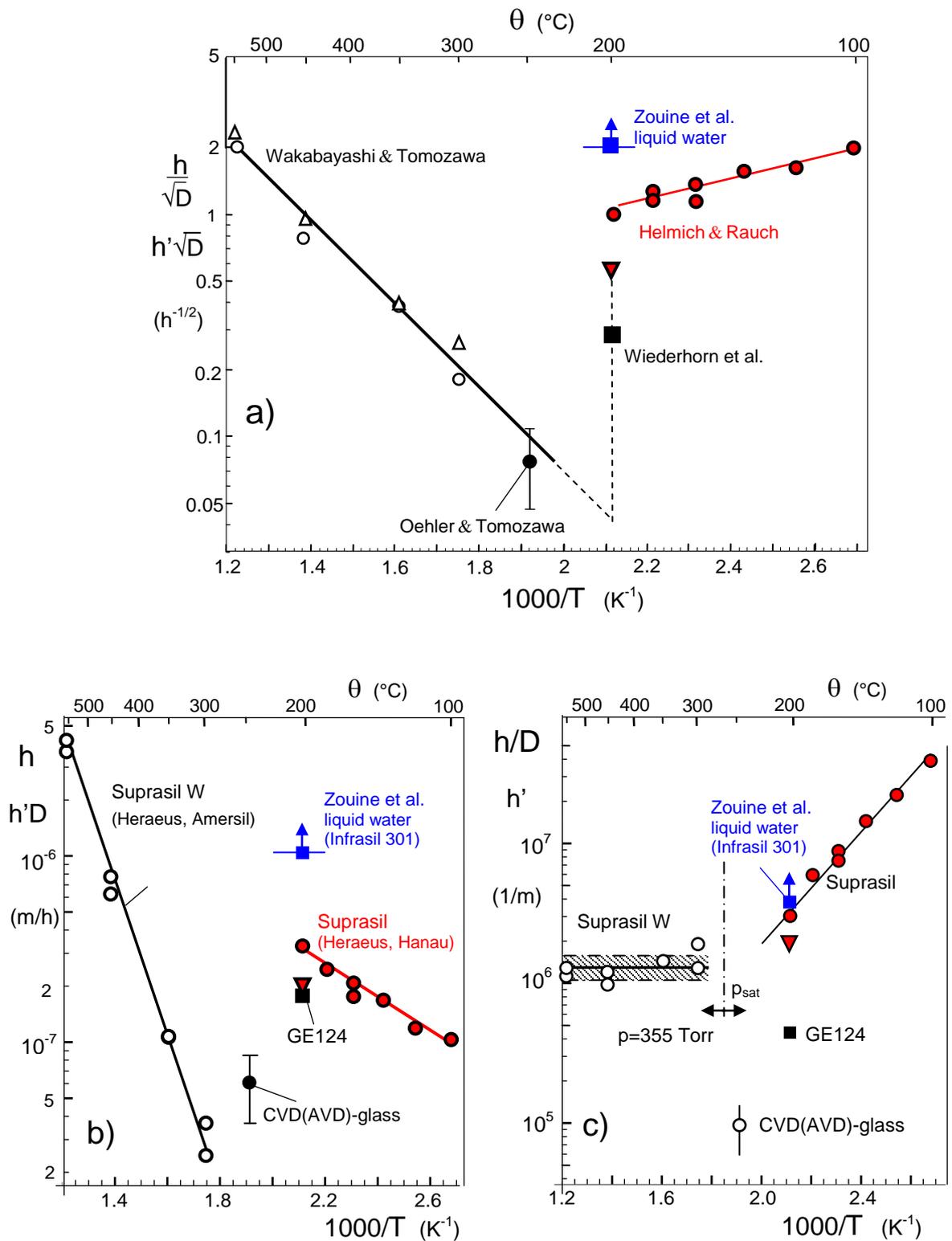


Fig. 3 a) Mass-transfer parameter h/\sqrt{D} as a function of temperature; triangles: evaluation by fitting of Heraeus Infrasil 301, (type-I fused quartz), b) mass transfer coefficient h , c) same data in the form of h/D .

3 Some possible reasons for different h

The question remains as to what influenced the data in Figs. 3a-3c and how the different results or the material “scatter” are caused. In this context some points may be mentioned to be studied in future work:

- a) Slightly different compositions of silica (weak doping or minor impurities).
- b) Individual nano-porosity due to the varying ring structure.
- c) Dissolution of the near-surface layers in water and corrosion [1,8].
- d) Surface enlargement due to roughness and corrosion.

The points a) and b) seem to be simple since it is trivial to assume that different materials can behave differently. Chemical composition is more likely to have less of an impact on material transfer than different ring structure and pore size distributions.

The point c) has been discussed in [1]. Let us therefore address point d) qualitatively, which has not been dealt in our previous reports.

In contact with water, silica reacts at the surface according to the equation



In liquid water, the H_4SiO_4 can dissipate from the surface by diffusion into the bulk water. In the case of water vapour, multilayer water exists only in the immediate vicinity of the surface. The formation of H_4SiO_4 in this small amount of water could severely limit material removal from the surface.

Equation (2a) assumes the existence of a smooth surface through which the water is introduced. This assumption is sufficiently fulfilled for glass samples stored in moist air at 200°C. In liquid water the dissolution and corrosion may be clearly stronger as is visible from surface measurements by Inniss et al. [15] (for detail see their Fig. 2b).

An increased surface area allows water to enter the glass more easily as has been outlined in literature (see e.g. [16-18]). Thus, Dawson and Trass [16] report that a rough surface can show an increase in h of 3-4 times that of a smooth surface.

Van Vliet and Young [17] report increased mass transfer by a factor of 7.5. These examples make it clear that the roughness of the surface can have a significant influence on h .

A further increase in the effective surface compared to the geometric surface (length x width of a macroscopic surface element) may be caused by the nano- and meso-pores, which can cause a significant increase in surface area depending on the frequency of their occurrence. Unfortunately, no detailed information is given on the surface-porosity after dissolution by Zouine et al. [9].

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ISSN 2194-1629

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