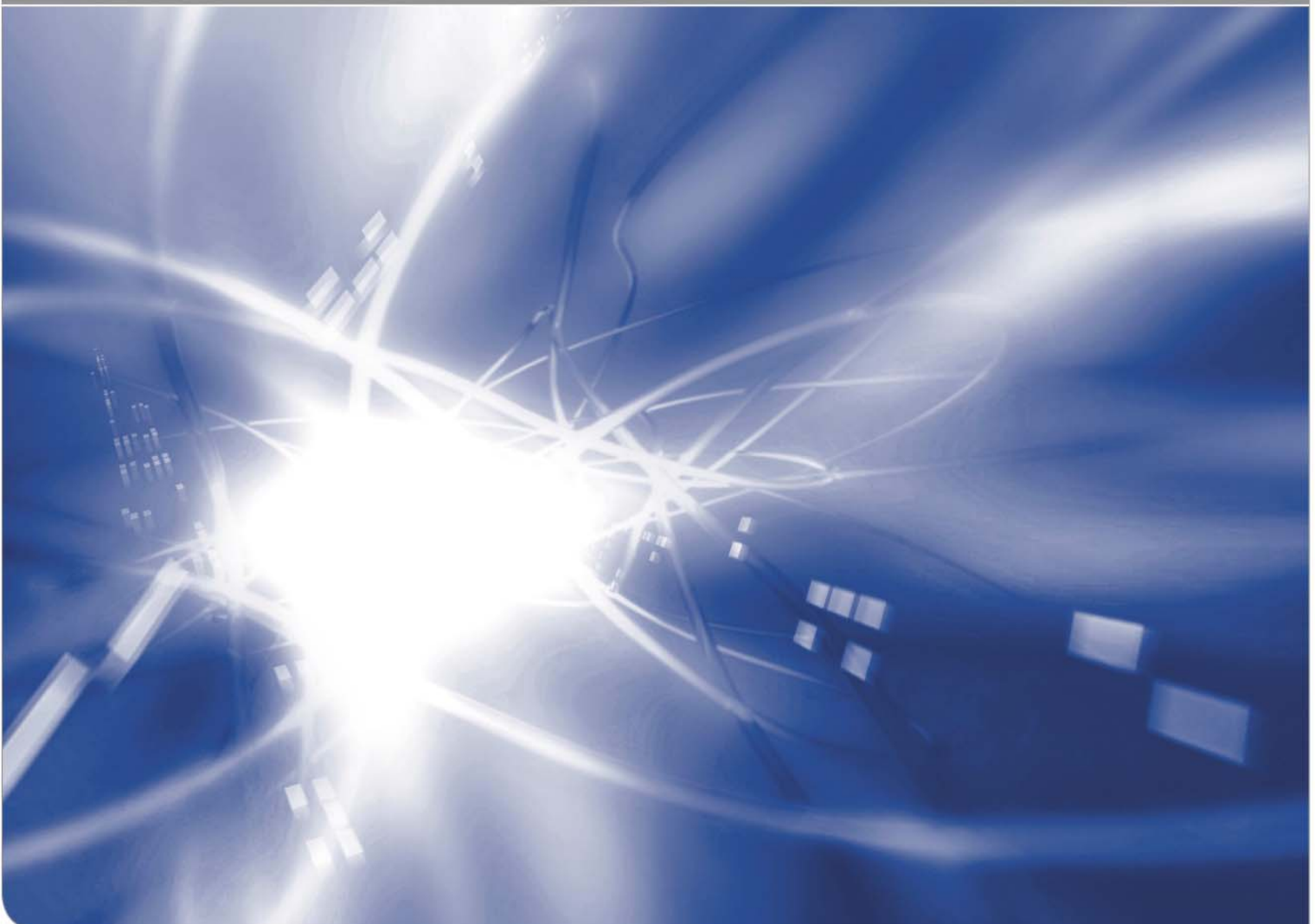


Distribution of equilibrium constant k and hydroxyl S in silica surface layers

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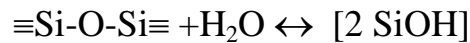
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Abstract

The concentration of water penetrated into silica depends strongly on the stress state in the surface region. In the water diffusion zone hydroxyl water is generated by the water/silica reaction that is at temperatures $<450^{\circ}\text{C}$ a first-order reaction. When $[2S]=[2\text{SiOH}]$ is the concentration of the immovable hydroxyl, the reaction equation reads



For this reaction the equilibrium constant is strongly affected by stresses, internal swelling stresses and externally applied stresses. Since no activation volumes for this first-order reaction are available in literature, we will show here the principal influence by a parameter study. As the main results we concluded:

- 1) With increasing reaction volume ΔV , the concentration of the hydroxyl $S(z)$ at the surface is significantly reduced and slightly increased inside.
- 2) The shape of the S -distribution deviates strongly from the profile of the total water concentration, $C_w(z)$.
- 3) The product of the "effective layer thickness" and the level of the S -concentration, $S(0)\times z_{\text{eff}}$, is largely independent of the assumed reaction volume.

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1 Basic equations

Water penetrated into silica reacts with the silica network according to



with the concentration of the hydroxyl $S = [\equiv\text{SiOH}]$ and that of the molecular water $C = [\text{H}_2\text{O}]$. The equilibrium constant of this reaction is at temperatures of $\theta < 450^\circ\text{C}$

$$k = \frac{S}{C} \quad (2)$$

Water concentrations at silica surfaces under saturation pressure are available from investigations by Öhler and Tomozawa [1] and Zouine et al. [2]. Since the Zouine data extend over the large temperature range of $23^\circ\text{C} \leq \theta \leq 200^\circ\text{C}$, these results may be applied in the following considerations.

In *molar units*, the total water concentration is given by

$$C_w = C + \frac{1}{2}S = C(1 + \frac{1}{2}k) \quad (3)$$

Equations (2) and (3) result in

$$C = \frac{C_w}{1 + \frac{1}{2}k}, \quad (4)$$

$$S = \frac{C_w}{\left(\frac{1}{2} + \frac{1}{k}\right)} \quad (5)$$

By density measurements, it was early shown by Brückner [3, 4], Shackelford [5] and Shelby [6] that the volume of glass increases with increasing water concentration that is due to the high temperatures of $\geq 1000^\circ\text{C}$ exclusively present in hydroxyl form. The volume expansion strain is proportional to the hydroxyl concentration

$$\varepsilon_v = \kappa \times S \quad (6)$$

In the case of thin water layers at glass surfaces where the glass cannot freely expand, compressive swelling stresses must be generated

$$\sigma_{sw,z} = \sigma_{sw,y} = -\frac{\varepsilon_v E}{3(1-\nu)} \quad (7)$$

with the hydrostatic stress term $\sigma_{sw,h}$ given as

$$\sigma_{sw,h} = \frac{1}{3}(\sigma_{sw,x} + \sigma_{sw,y} + \sigma_{sw,z}) = -\frac{2\varepsilon_v E}{9(1-\nu)} \quad (8)$$

From the work of Le Chatelier [7], it is well known that chemical reactions that exhibit a change in volume will be sensitive to the ambient pressure of the reaction. Changing the pressure, p , changes the equilibrium constant of the reaction and hence the ratio of the concentration of reaction products to reactants. The equation governing the reaction is

$$\frac{\partial \ln k}{\partial p} = -\frac{\Delta V}{RT}. \quad (9)$$

k is the equilibrium constant, p is pressure, ΔV is the reaction volume, R is the universal gas constant and T is the temperature in °K. The reaction volume ΔV can reach high values [8] for temperatures $<450^\circ\text{C}$ and may be different in the temperature regions of $<450^\circ\text{C}$ (first-order reaction) and $>450^\circ\text{C}$ (second-order reaction).

When $[2S]=[2 \text{ SiOH}]$ is the concentration of the immovable hydroxyl, the reaction equation (1a) reads



In this case the equilibrium constant for the reaction under hydrostatic pressure is

$$\Delta V = \bar{V}_{[2S]} - \bar{V}_C. \quad (10)$$

with the partial molar volume for $[2 \text{ SiOH}]$, denoted by $\bar{V}_{[2S]}$.

In a solid the situation is more complicated, since the individual stress components σ_x , σ_y , σ_z are in general independent of each other. The equivalent for the pressure is the hydrostatic stress term, $\sigma_h = -p$, that allows to write eq.(9) as

$$\frac{\partial \ln k}{\partial \sigma_h} = \frac{\Delta V}{RT}. \quad (11)$$

In the absence of externally applied stresses, it is $\sigma_h = \sigma_{sw,h}$. Then the equilibrium constant reads according to [9]

$$k = k_0 \exp\left(-\lambda \frac{S\Delta V}{RT}\right) \quad (12)$$

with $\lambda=18.8 \text{ GPa}$. The hydrostatic stress reads

$$\sigma_{sw,h} = -\lambda S \quad (13)$$

The equilibrium constant as a function of the measured C_w finally results from (12) and (5) in the implicit equation

$$k = k_0 \exp\left(-\frac{\lambda \Delta V}{RT} \frac{C_w}{\frac{1}{2} + \frac{1}{k}}\right) \quad (14)$$

since k is present on the left-hand side as well as on the right-hand side in the denominator of the exponential function.

In the same way, we obtain also an implicit equation for the hydroxyl concentration

$$S = \frac{C_w}{\left(\frac{1}{2} + \frac{1}{k_0} \exp\left[\frac{\lambda \Delta V S}{RT}\right]\right)} \quad (15)$$

It is obvious that the equilibrium constant varies in a water diffusion zone where C_w varies with depth and an average value \bar{k} over the depth profile.

$$\bar{k} = \frac{\bar{S}}{\bar{C}} = \frac{\int S(z) dz}{\int C(z) dz} \quad (16)$$

The value k is mostly obtained in literature by transmission IR measurements of hydroxyl and molecular water. These measurements reflect average values \bar{k} over the whole water profiles, $0 \leq z \leq W$.

The equations (14) and (15) contain two unknown parameters, namely k_0 and ΔV which have to be determined by measurements. These values are not freely eligible. They are interrelated by the known value of \bar{S}/\bar{C} , see [10].

The experimental results on equilibrium ratios from literature were expressed in [11] for the temperature range of $90^\circ\text{C} \leq T \leq 350^\circ\text{C}$ by the empirical relation

$$\bar{k} = \frac{\bar{S}}{\bar{C}} = A \exp\left(-\frac{Q}{RT}\right) \quad (17)$$

($A=32.3$ and $Q=10.75$ kJ/mol).

In *mass units* it is

$$S = \frac{17}{18} \frac{C_w}{\left(\frac{1}{2} + \frac{1}{k}\right)} \quad (18)$$

(the ratio 17/18 reflects the different mole masses of water and hydroxyl).

Figure 1a gives the total water concentration in mass units in a plot with the temperature θ as the linear abscissa. The straight line gives

$$C_w = 0.000780 \exp(0.00868 \theta) \quad (19)$$

Figure 1b illustrates the S -data in a similar plot with a slightly curved averaging curve given by

$$S = \frac{17}{18} \frac{0.000780 \exp(0.00868 \theta)}{\frac{1}{2} + \frac{1}{A} \exp(Q/RT)} \quad (20)$$

again with the parameters $A=32.3$ and $Q=10750$ J/mol

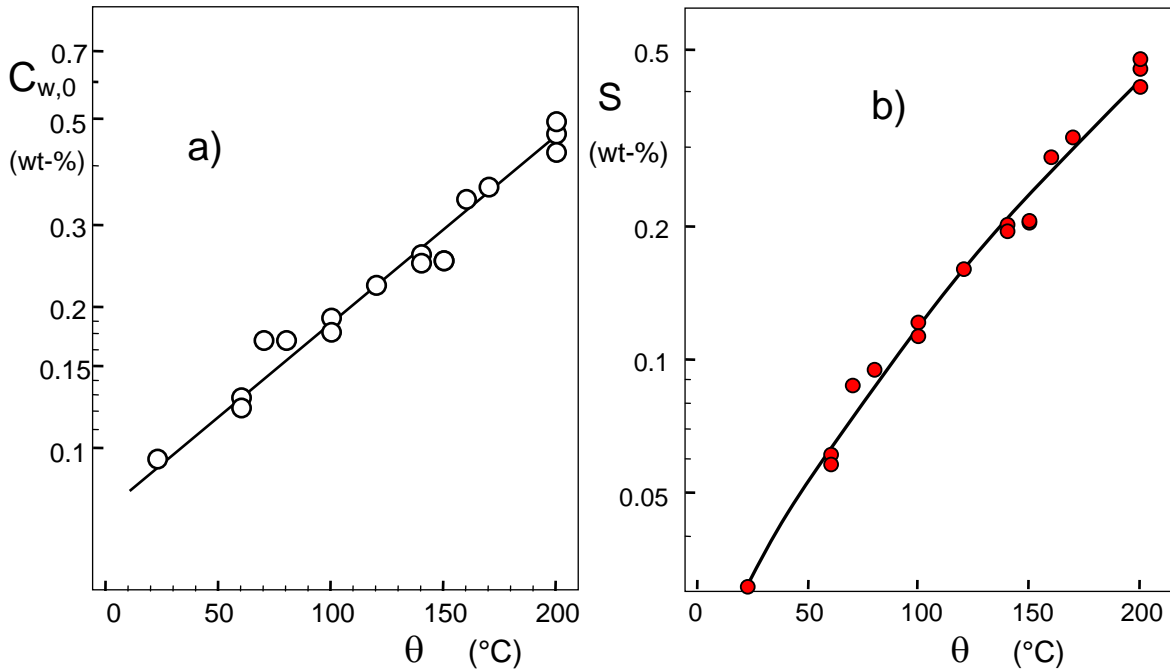


Fig. 1 Total water and hydroxyl data plotted with linear abscissa scaling, a) total water, b) hydroxyl water concentration, curve: eq.(20).

2 Depth profiles

2.1 Effect of swelling stresses on hydroxyl concentration for 200°C

Equation (14) makes clear that a depth profile $C_w=f(z)$ of total water must result in a profile of the equilibrium constant k . Very often the measured total water profiles are given by (see e.g. [2])

$$C_w = C_w(0) \operatorname{erfc}\left(\frac{z}{2b}\right) \quad (21)$$

In the absence of experimental data for the reaction volume ΔV at temperatures $< 450^\circ\text{C}$, we carried out a parametric study that at least shows the influence of the reaction volume in principle. In doing so, we were aware that the reaction volume of the first-order reaction could certainly assume a high value, [8].

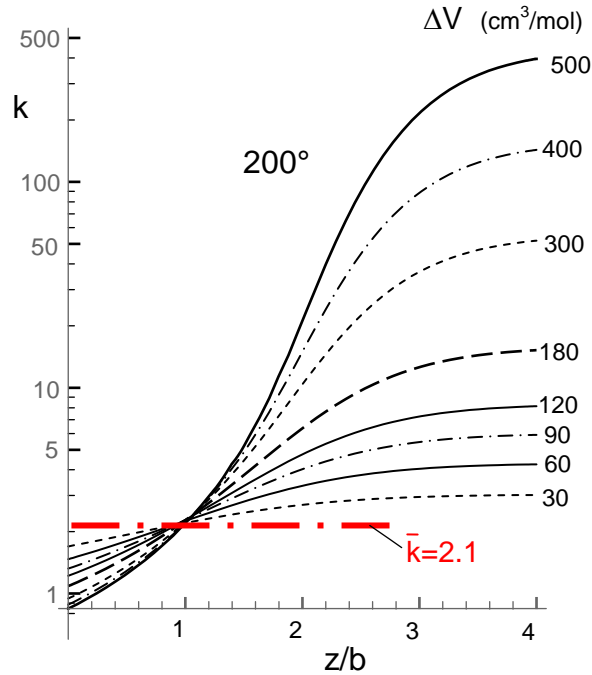


Fig. 2 Distribution of the equilibrium constant k in the silica surface for 200°C .

First we solved eq.(14) with respect to the equilibrium constant k for 200°C by using the numerical *Mathematica*-Routine *FindRoot* [12] under the condition of $\bar{k} = 2.1$ as is given by eq.(17). The resulting set of curves $k=f(z/b, \Delta V)$ are plotted in Fig. 2 for differently chosen reaction volumes. The “average” equilibrium constant, $\bar{k} = 2.1$, is indicated in Fig. 2 by the red line. This line represents also the equilibrium constant for the case of a disappearing reaction volume, $\Delta V=0$.

Then, the hydroxyl concentration profiles $S=f(z/b, \Delta V)$ could be obtained from eqs.(18) and (21). Figure 3a shows the results of S normalized on the surface value S_0 of the surface hydroxyl water concentration for $\Delta V = 0$ and a temperature of 200°C . Figure 3b additionally shows the results for 100°C (blue curves) where the boundary condition now reads $\bar{k} = 1.1$. The dashing of the curves corresponds to the same reaction volumes as in the case of 200°C .

All results show a strong variation of the local equilibrium constant $k(z)$.

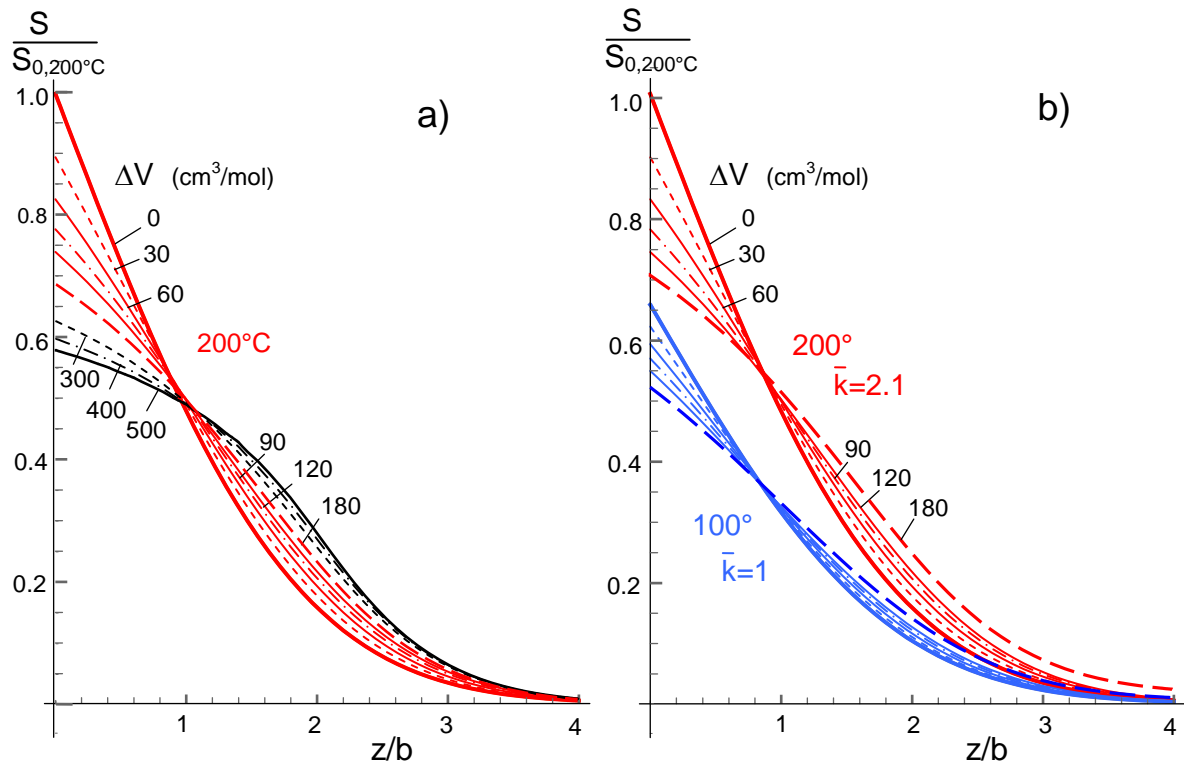


Fig. 3 Distribution of hydroxyl concentration S in the silica surface, a) for 200°C and a wide range of the activation volume, b) comparison of results for 100° and 200°C.

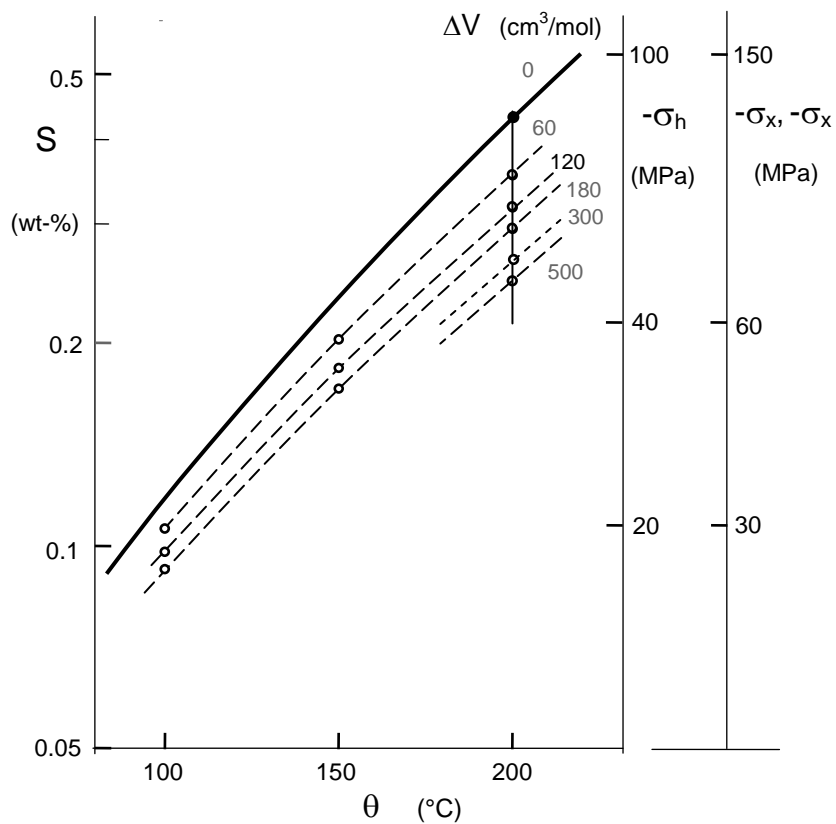


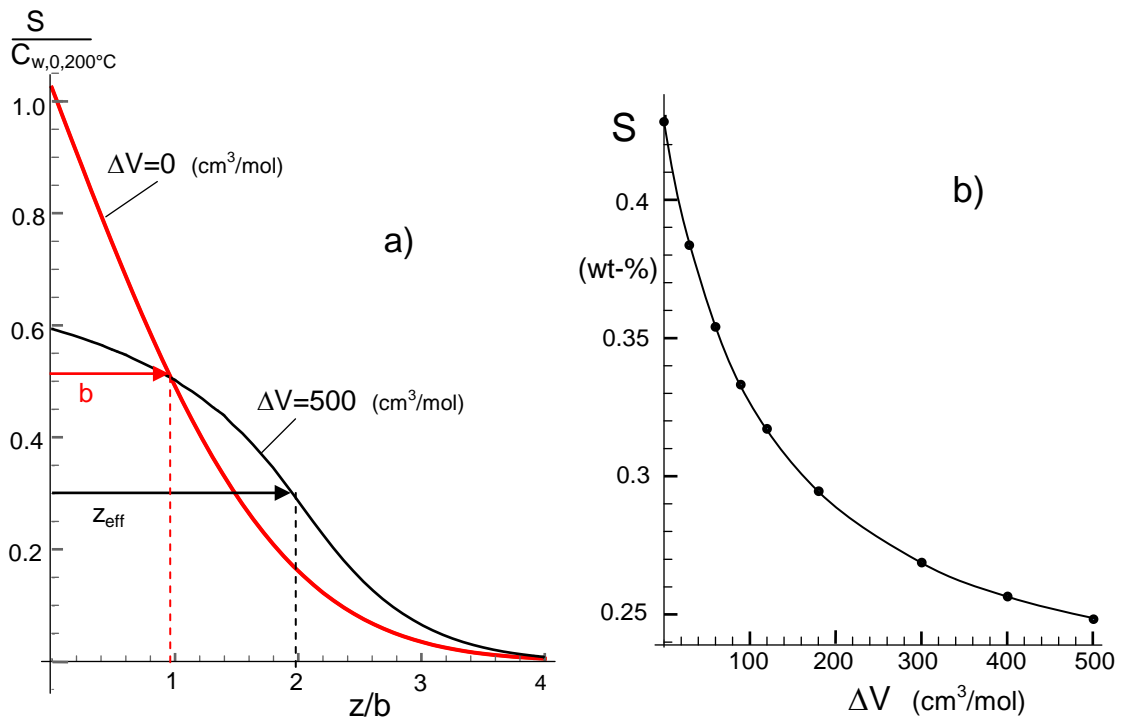
Fig. 4 Effect of swelling stresses on hydroxyl concentration at the surface (left ordinate) and the related hydrostatic and linear swelling stresses (right ordinates).

2.2 Hydroxyl concentrations depending on temperature

The data of Fig.1 b represented by the solid line for $\Delta V=0$ are plotted in Fig. 4 together with the curves for a number of reaction volumes. Whereas the left ordinate shows the hydroxyl concentrations at the surface, the right ordinates represent the related hydrostatic and equi-biaxial swelling stresses according to eqs.(7) and (8). A clear decrease of the stresses is visible for an increasing reaction volume. The S-curves, strongly deviating from the erfc-shaped total water distribution, give rise for an effective layer thickness b_{eff} as is defined by the depth in which the concentrations are reduced to 50% of the surface values.

2.3 Numerical results

Figure 5 summarizes the results of the numerical computations. From the example in Fig. 5a it can be seen, that the layer width increases by a factor of about 2 with ΔV increasing from 0 to 500 cm^3/mol . Simultaneously, the surface S-concentration and the swelling stresses decreased as is visible from Fig. 4. Figure 5b shows the surface S-concentration at 200°C and Fig. 5c the related layer thicknesses b_{eff} , both depending on the reaction volume ΔV . Finally, Fig. 5d gives the product $b_{\text{eff}} \times z_{\text{eff}}$ as a result of the reaction volume. This quantity also represents in principle the mechanical bending moment that is caused by the swelling stresses. The solid line indicates the average value over the wide region of parameter ΔV and the dash-dotted lines show ± 1 SD (SD=Standard Deviation).



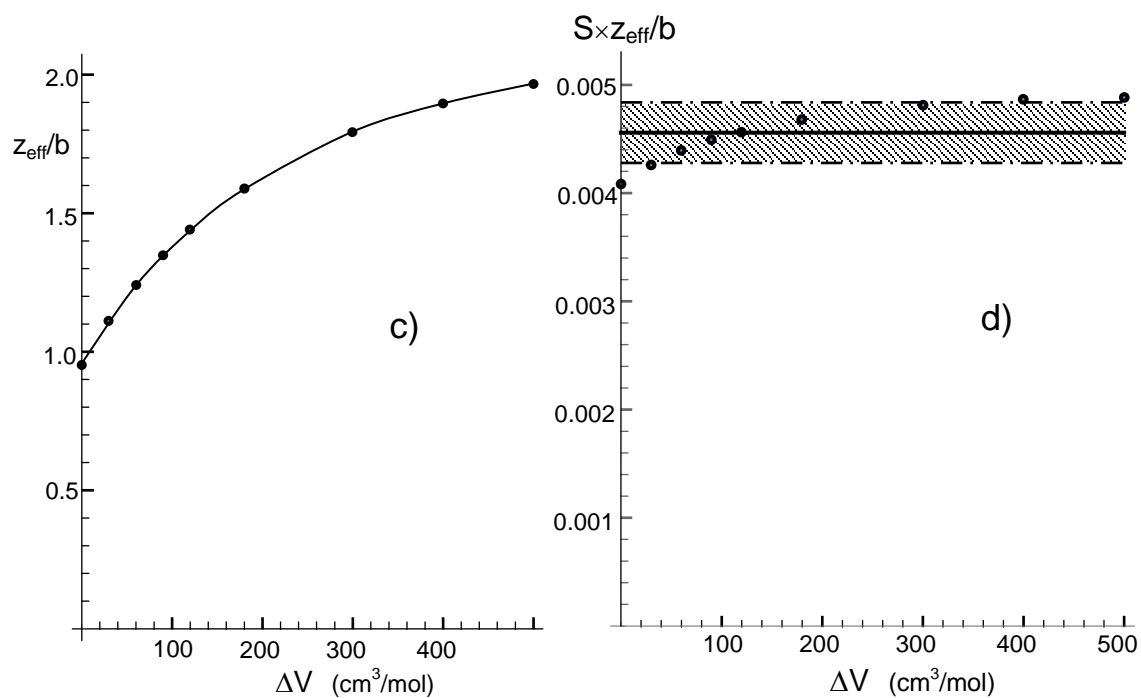


Fig. 5 Influence of swelling on the maximum concentrations and half-width b_{eff} of the profiles, a) definition of an effective layer thickness z_{eff} , b) S -concentration at the surface $z=0$, c) effective zone thickness, d) product of surface concentration and effective layer width, representing bending moment due to water uptake.

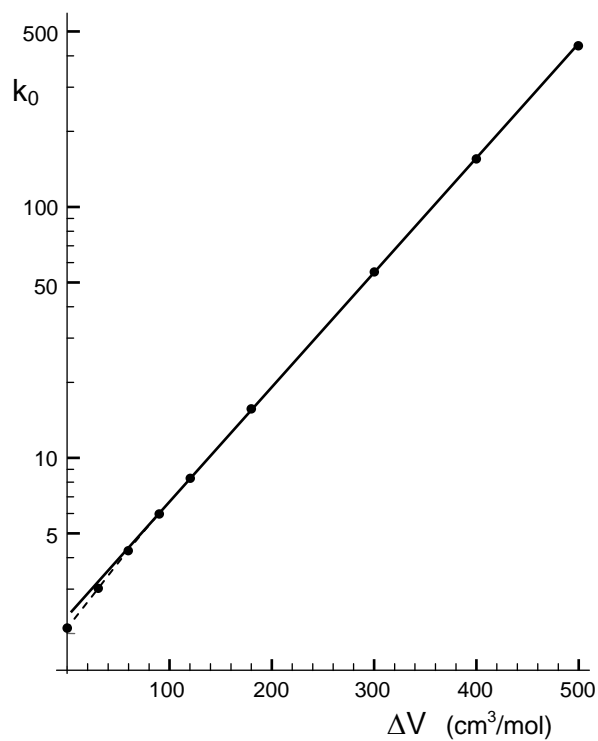


Fig. 6 Numerical dependency between the parameters k_0 and ΔV for 200°C

Finally, Fig. 6 shows the numerically obtained dependency between the parameters k_0 and ΔV . For $\Delta V > 60 \text{ cm}^3/\text{mol}$ it can be written

$$k_0 \cong A_1 \exp[A_2 \Delta V] \quad , \quad (22)$$

with $A_1=2.337$, $A_2=0.010485 \text{ mol}/\text{cm}^3$, represented by the solid straight line in Fig. 6.

3 Conclusions

The main results of the present parameter study on the influence of the swelling stresses on the depth profiles of the hydroxyl concentration $S(z)$ can be summarized as follows:

- 1) With increasing reaction volume ΔV , the concentration of the hydroxyl $S(z)$ at the surface, $z=0$, is significantly reduced and slightly increased inside (for $z>b$).
- 2) The shape of the S -distribution deviates strongly from the profile of the total water concentration, $C_w(z)$.
- 3) The product of the "effective layer thickness" and the level of the S -concentration, $S(0) \times z_{\text{eff}}$, is largely independent of the assumed reaction volume. This influence has the potential to interpret the experimental finding of agreement between water absorption and bending moment as well as the relatively low absolute value of the threshold stresses at the surface [11]. This will be shown in a separate report.

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