Modeling of glass corrosion – improvement of the constitutional model

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A model based on the constitutional relations within the respective crystalline reference systems of glasses, on their Gibbs energy of hydration, and on the pH-dependent surface coverage of SiO_2 has been used with success to predict the chemical durability of different glass compositions in various aqueous exposure scenarios. In the present paper, the model is improved in three areas. Firstly, the temperature dependence of all quantities used is revised in a thermodynamically consistent way. Secondly, the surface equilibrium established instantaneously at an exposed glass surface is investigated. It is this equilibrium which allows to convert pH and composition dependent glass stabilities (as reflected by Gibbs energies of hydration) into pH dependent dissolution rates. The concept of surface coverage is extended to multicomponent surfaces by using the concept of point of zero charge. Finally, the constitution of hydrated sub-surface layers is investigated. Their stoichiometries are predicted by the phase diagrams of corresponding silicate-H_2O systems, which are constructed from scattered literature data. All conclusions are substantiated by experimental results.

The concept of the constitutional compounds

The concept of constitutional compounds as a crystalline reference state was firstly applied to explain the structure of glasses[1] but turn out to be useful to predict glass corrosion, too[2]. For this purpose, the thermodynamic state of the glass is calculated by the Gibbs energy of formation ΔG_{gl} of its compounds *k* referring to the crystalline reference state by the vitrification energy G^{vit}. The second quantity is the Gibbs energy of formation of the aqueous system from the oxides (in portions as contained in the glass) and the initially unaltered solution. The difference between the Gibbs energy of formation of the glass ΔG_{gl} and the Gibbs energy of the dissolved aqueous species ΔG_{aq} is called Gibbs energy of hydration ΔG_{hydr} which is an indicator for the thermodynamic force of corrosion tendency.

$$\Delta G_{hydr} = \Delta G_{gl} - \Delta G_{aq} = \sum_k \left(x_k \cdot G_k + x_k \cdot G^{vit} \right) - \sum_k x_i \cdot G_i \qquad (1)$$

where x denotes the molar fraction (for calculation details see [3]). Dissolution rates can be calculated by the equation of the mineral dissolution by Aargard and Helgeson [4] extended by the surface coverage Θ by ions of the aqueous solution (for details see [3]):

$$\log r = \log r_X - \frac{\beta \cdot M_{SiO_2} \cdot \Delta G_{hydr}}{2.3 \cdot 4 \cdot x_{SiO_2} \cdot R \cdot T} + (1 - \beta) \cdot \log \Theta \quad . \qquad (2)$$

In eq. (2) M is the molar weight, r the rate, β is a transition coefficient, and Θ the surface coverage. In order to improve the existing model of the constitutional compounds, it was applied to materials with exotic compositions, e.g. the phosphate glass KG1 and the partial crystalline ZERODUR®. Glass compositions of alumoborosilicate glasses in the system Na_2O-Al_2O_3-B_2O_3-SiO_2 were also investigated. The results of the model (figure 1a to c) are in good agreement with the experimental data, even for the non-silicate glass and the partial crystalline material.

Temperature dependence of glass dissolution

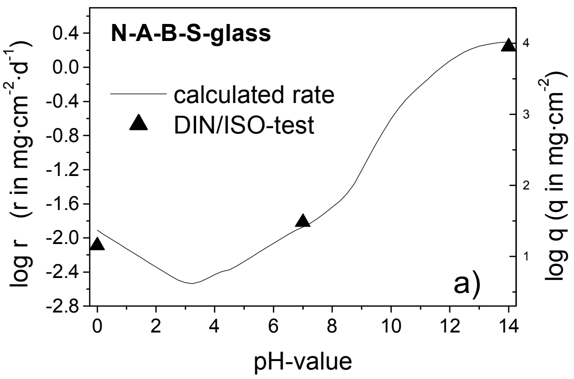
For calculating the temperature dependence, sufficient tabulated thermodynamic data of solid phases are available. In contrast to the solid state, Gibbs free energies of formation of the aqueous ions as a function of temperature a rare. Therefore the concept of Criss and Cobble[5] based on the correspondence principle of entropies was introduced in the model. The entropy of a substance corresponds to properties like ion charge z, radius of the ion r_{ion}, its mass m, its dielectric constant ε, and the temperature T:

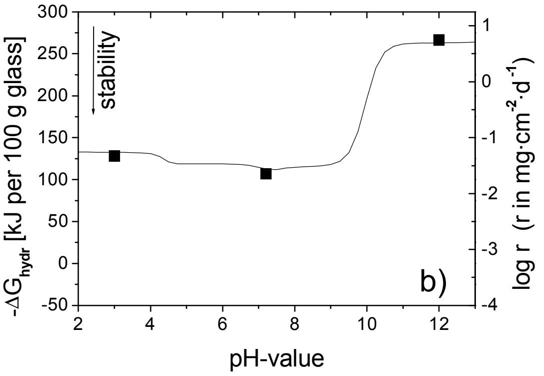
$$S_T^0 = f(z,\ r_{ion},\ m,\ \varepsilon,\ T,...) \quad . \tag{3}$$

Knowing the correspondences for the individual ions, it is possible to calculate a temperature dependency by a linear interpolation. The temperature 25 °C and the ionization energy of the hydrogen atom are used as the reference state. Criss and Cobble subdivided all ions in four classifications following the relation

$$S_T^0 = a_c(T) + b_c(T) \cdot S_{T_R}^0 \quad , \tag{4}$$

where S denote the entropy, a and b temperature coefficients depending on the ion classification, and T_r the reference state (for calculation details see [6]). By this proceeding, the calculation of free energies of aqueous species at specific temperatures are assessed. Results of the calculation of the solubility of SiO_2 in water and in sodium containing water are presented in figures 2a and b. In both figures the stability of SiO_2 show a good agreement with the experimental data. In sodium containing solutions the surface coverage has a significant impact on the SiO_2 solubility following eq. (5).





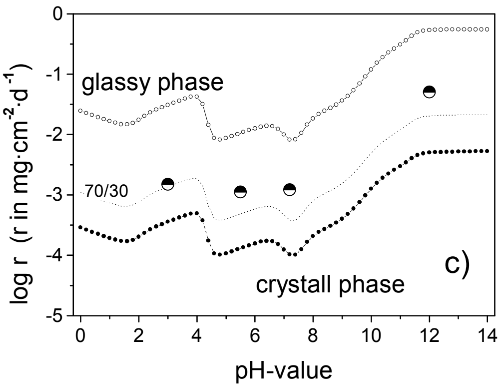


Fig 1. Comparison between calculated corrosion properties and experimental data: a) alumoborosilicate glass versus DIN/ISO tests; b) calculated free energies of hydration of the phosphate glass KG 1 versus experimental dissolution rates; c) calculated and experimental dissolution rates of ZERODUR®

$$\log\Theta = \sum_{Y} \frac{k_Y \cdot c_Y}{1 + k_Y \cdot c_Y} \tag{5}$$

with *c* denoting the concentration, Y the species H^+, OH^-,and Na^+. For the sodium adsorption coefficient $k_{Na+} = 1.6 \cdot 10^{-9}$ was used. Since the solubility of SiO_2 is strongly dependent on the sodium adsorption, more tests on the adsorption behavior of metal ions on glass surfaces have to be conducted.

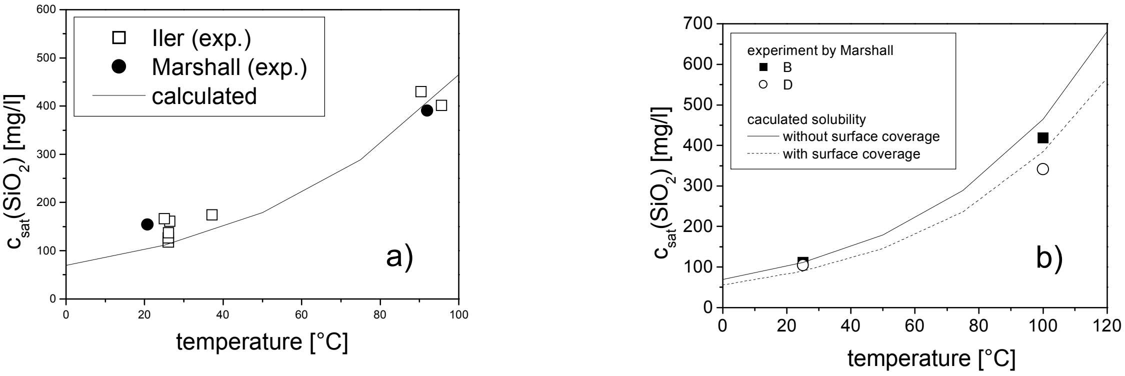


Fig 2. Temperature dependence of the SiO_2 solubility

Interaction at the water-glass-interface

Baucke[7] investigated the glass pH-electrode and concluded that there is a very fast initial process, where electrochemical reactions are equilibrated. This basic idea is included in eq. (5) by the surface coverage Θ which can be described by eq. (5) for all aqueous species. The main characteristic function of the surface coverage is the point of zero charge. For all substrates exposed to water at a specific pH value, the concentration of adsorbed positive ions equals the adsorbed negative ions, this pH value is called point of zero charge (pH_{PZC}). Knowing the pH_{PZC} the surface coverage of glasses can be easy estimated.

For the prediction of pH_{PZC} of multicomponent oxide compositions, the concept of Sverjensky[8] was adapted to glasses. The pH_{PZC} is calculated by the dielectric constant ε of the glass and the mean corrected Pauling bond strength (s_C/r_{M-OH}) by

$$pH_{PZC} = 21.1158 \cdot \frac{1}{\varepsilon} + 42.9148 \cdot \frac{s_C}{r_{M-OH}} + 14.6866 \quad , \tag{6}$$

where s_C denotes the ratio between the charge and the coordination number of the metal ion and r_{M-OH} denotes the bond length of the metal ion to hydroxid group. Especially for basalt glasses or glasses with high basicity the influence of pH_{PZC} on the glass corrosion is significant. Fig 3a shows the calculation of the surface coverage Θ for different glass compositions. Θ is proportional to the concentration of H^+ and OH^- and is assumed to reach the concentration of a pure SiO_2 surface at the pH_{PZC}. The immobilization of adsorbed species at the pH_{PZC} is high. As a consequence, the term Θ in eq. (5) is extended by the reverse function of the Lennard-Jones potential:

$$\Delta(\log\Theta) = -\frac{1}{\left|pH_{PZC} - pH\right|^{\frac{1}{6}}} \qquad . \qquad (7)$$

Fig. 3a shows that only the basalt glass reaches a complete surface coverage with H^+ at low pH. Exploiting the prediction of pH_{PZC} the corrosion properties of two different glasses are calculated and displayed in fig. 3b.

The calculated results show the same pattern as the experimental data. However, deviations of some data points are given. Thus, in order to improve the prediction concept of pH_{PZC}, more experimental tests on the ζ-potential have to be conducted and compared to the effects of glass corrosion. Since the electrochemical equilibria are adjusted very quickly and cause glass corrosion, the tests on ζ-potentials have to be conducted very carefully.

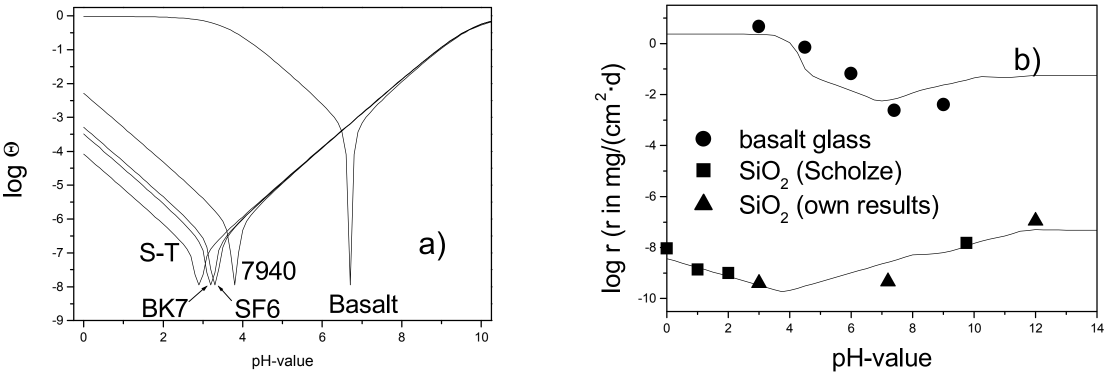


Fig. 3. Surface coverage of different glass compositions (a) and calculated and experimental dissolution rates of two different glasses (b)

Constitution of the sub-surface layer

During the glass corrosion process, an altered sub-surface zone (termed gel layer) is formed in most cases, which is a consequence of incongruent dissolution. This sub-surface zone contains considerable amounts of water. According to the model of the constitutional compounds, the gel layer may have a crystalline reference different from the bulk glass. Roggendorf[9] who investigated water glasses found that modeling the corrosion properties with constitutional compounds of the bulk glass was not successful. The authors of the present study came to the conclusion that this kind of difficulty will occur in all cases where the amount of water incorporated in the glass matrix shifts a glass towards a crystalline reference state definitely different from the bulk. For the sake of clarity: This has nothing to do with the gradual composition changes brought about by diffusion (which is a secondary process running between the Gibbs energy niveaus (better: chemical potential) of the bulk and of the very glass surface). Rather, this refers to a shift of the niveaus of the bulk towards a different state. In order to demonstrate the idea, a phase diagram H_2O-Na_2SiO_3 was developed after fig. 1959 to 1963 from [10]. The complex phase relations are illustrated in fig 4a. Following this phase diagram a corroded binary sodium silicate glass should have an alterated surface layer reflecting the sequence of sodium hydrate-silicate from dry NS to NSH_9.

In fig. 4b experimental data of Smets and Lommen[11] are evaluated with respect to the results of the phasediagram in fig. 4a. The linear regressions of the sodium surface content (analyzed by SIM) show kinks at the theoretical phase boundaries which is in good agreement with the above prediction.

This concept also opens the door to describing the composition of the sub-surface layers.

To improve the concept of surface constitution for the mass glasses the access to phase diagrams of the type H_2O-CaO-MgO-Al_2O_3-SiO_2, Na_2O-Al_2O_3-B_2O_3-SiO_2, and H_2O-K_2O-PbO-SiO_2 is necessary. Bowers et al.[12] calculated a wide range of activity diagrams of mineral solutions. For application of these diagrams the data collected in corrosion experiments should comprise more details. In specific, solution analysis is needed to correlate the diagrams with the surface constitution.

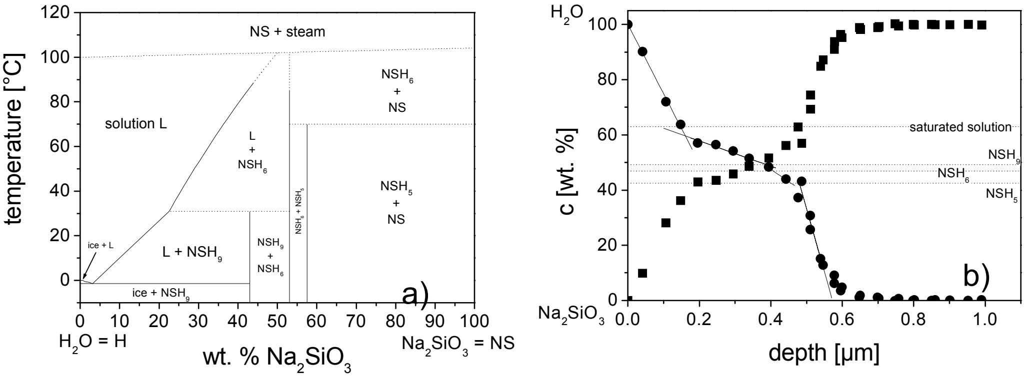


Fig. 4 The system Na_2O-SiO_2-H_2O.

a) the developed phasediagram after [10] b) the experimental evidence of the developed phasediagram; closed lines: linear regression of the surface composition; dashed lines: theoretical phase boundary according to a); data: [11]

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