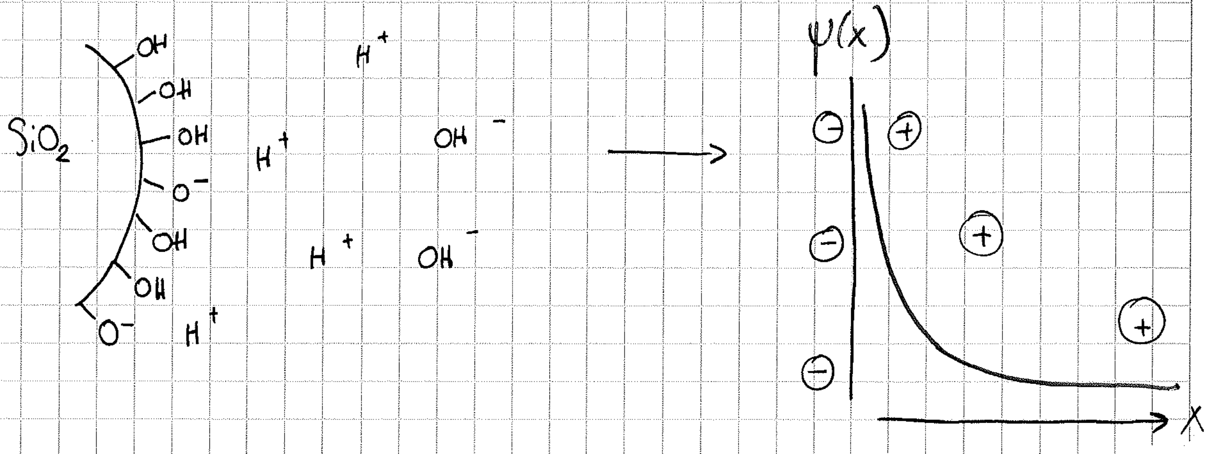
Solutions exercise 24

a) At pH 7, we can expect the following chemical equilibrium:

$$SiOH \longrightarrow SiO^- + H^+$$

On average, we only have 1% of the total SiOH groups that are deprotonated. Because we have not added other ions to the system, the only ions present are the $[H^+]$ counterions from the deprotonation reaction, and the ions corresponding to the auto dissociation of water (at pH 7, $[H^+]_{H_2O} = [OH^-]_{H_2O} = 10^{-7}$ M). The total concentration of ions in solution is therefore quite low, and one can use the Gouy - chapman model to describe the system:



b) At higher ionic strength, both the Gouy - Chapman - Stern model and the Grahame model could be used to sketch the situation.

	CHARACTERISTICS	ASSUMPTIONS
GCS	• Combination of a $\overset{\text{STERN}}{\text{“capacitor”}}$ layer and a diffuse layer • ψ_0 decay is approximated to a linear decay up to the Stern plane, and an exponential decay in the diffuse layer • Used usually for higher potential values and higher ionic strengths	• Stern layer is thin: 1 - 3 water molecules • Often considered that the fluid velocity with respect to the surface is zero within the Stern layer.

	CHARACTERISTICS	ASSUMPTIONS
GRAHAME	• Considers finite ion size and hydration sphere • Inner Helmholtz plane: ions are partially dehydrated and adsorbed @ the surface • Outer Helmholtz plane: Similar to a Stern layer • Apparent ψ_0 can be decreased by specific ion adsorption	• Similar to above

c) We assume that the position of the slipping plane corresponds to the position of the Stern plane, i.e: $\zeta = \psi_{stern}$.

Additionally, $\sigma_s = 90\% \times \sigma_0$.

$$\psi_0 = \frac{\sigma_S \, d_{stern}}{\varepsilon_0 \varepsilon_{SiO_2/water}} + \psi_{stern}$$

$$= \frac{\sigma_S \, d_{stern}}{\varepsilon_0 \varepsilon_{SiO_2/water}} + \zeta = \frac{-0.009/m^2 \times 0.9 \cdot 10^{-9} \, m}{8.85 \cdot 10^{-12} \times 43} - 0.05 V$$

$$\simeq 71 \, mV$$

d) Here, ΔG_{hyd} gives an estimate of the energy necessary to reorient the polar solvent molecules around the ion with respect to the state of randomly oriented dipoles. In practice, it gives an indication on how much energy is necessary to disrupt the hydration shell of the ion. One can see that it requires less energy to remove water molecules from the hydration shell of the sodium ion than from the calcium ion. This means that Na^+ is more susceptible to adsorb at the SiO_2 surface as a partially dehydrated (inner-sphere) ion.

e) The Na^+ ion is more susceptible to adsorb at the SiO_2 surface. For the same number of ions in solution (same concentration), the Na^+ ion will contribute to a greater decrease of surface potential, as ion adsorption partially "neutralizes" the surface charge density.

Exercise 25

a) Calculating the ionic strength for the three pH cases gives:

- pH = 2 corresponds to 10^{-2} M of HCl
  I (HCl) = 0.5 x 1^2 x 0.01 + 0.5 x 1^2 x 0.01 = 0.01 M

- In the pH = 7 case, the solution contains 10^{-2} M of NaCl
  I (NaCl at pH 7) = 0.5 x 1^2 x 0.01 + 0.5 x 1^2 x 0.01 = 0.01 M

- pH = 12 corresponds to 10^{-2} M of NaOH
  I (NaOH) = 0.5 x 1^2 x 0.01 + 0.5 x 1^2 x 0.01 = 0.01 M

b) The SiO_2 surface is not charged at pH = 2. With increasing pH, the SiO_2 surface becomes increasingly negatively charged due to the deprotonation of the Si-OH groups. In absence of specifically adsorbed ions, the larger the surface charge density, the higher the surface potential, regardless of the model used to estimate the surface potential. However, at very high pHs, there could be a competition between the increase in surface charge density due to the deprotonation reaction and a compression of the Stern layer due to the high concentration of NaOH that is not consumed in the deprotonation reaction. The latter effect would decrease the surface potential. This is not visible in Fig.2 up to pH = 12.

c) The average surface charge density is zero at pH = 2, but the local surface charge density can be very different. This reflects how heterogeneous "real" surfaces can be.

d) The experiment shows that the structure of the capillary is heterogeneous on a micron length scale, with patches that have vastly different surface potentials, and as a consequence, different surface chemical reaction equilibria constants for the deprotonation reaction. This shows there is a complex surface charge distribution varying across the interface that drives an ionic flux (of all ionic species) along the surface plane. This ionic flux in turn influences the chemical conversion of the silica groups with pH change. The establishment of the local chemical reaction equilibria occurs on a much slower time scale than the timescale of the liquid refreshing at every point of the system. Areas with a high reactivity will convert more quickly into other species (high energy states are shorter lived). These higher energy states exist on a 1s timescale, but they vanish over a 5s timescale.