

5.2. Elemental stoichiometries of amphoteric $\equiv\text{OH}$ functional groups

The 2-pK SCMs assume that oxide surfaces expose the *neutral amphoteric* $\equiv\text{OH}^\circ$ *functional groups* which can react with aqueous species via (de)protonation, exchange with anions, or binding of aqueous cations as the outer- or inner-sphere surface complexes [5, 71].

If the elemental stoichiometry and the formation reaction of the functional group were established, then the standard-state chemical potential μ° (or standard partial molal Gibbs energy g°) of those could be determined using the appropriate conventions on standard and reference states. Accordingly, this would make it possible to calculate g° values for all other surface species from equilibrium adsorption constants K_S (or the other way round). This is a key issue in our adsorption modeling approach which is not based on the site balance constraint. In other (site balance based) SCMs, the stoichiometry and g° value of the $\equiv\text{OH}$ group are not used, they are irrelevant and can be fixed *ad hoc*, e.g. taking $g^\circ = 0$ for the “SOH” species.

From several lines of reasoning presented above, it follows that *the activity of surface site (site species) is constant*, but (in the surface monolayer concept) its concentration (actual density) must give in upon adsorption of ions to provide the place for surface-bound complexes. There are two alternative lines of reasoning.

(1) If surface sites are viewed as part of the mineral sorbent of a fixed elemental composition then their activity will be the same as that of the solid (i.e. unity) indifferent of its amount and surface area, as long as it is present in the equilibrium state. The binding reaction of B in this case can be written as solid *site* + $\text{B}_{\text{aq}} \leftrightarrow \text{B}_{\text{ads}}$ with the LMA expression

$K_{S,B} = \frac{\{\text{B}_{\text{ads}}\}}{\{\text{site}\}\{\text{B}_{\text{aq}}\}}$. Assuming the activity of binding sites $\{\text{site}\} = 1$, this reaction can be simplified:

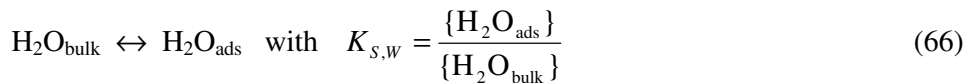


From Eq.(64), it is clear that K_{SB} is a kind of equilibrium constant for the species transfer from one phase to another; the “infinite dilution” reference state is appropriate; and it makes sense to consider B_{ads} in the same standard concentration scale as B_{aq} , i.e. in the molal scale. The Gibbs energy effect of reaction Eq. (64) then is

$$\Delta_r G_{S,B} = g^\circ(\text{B}_{\text{ads}}) - g^\circ(\text{B}_{\text{aq}}) = -RT \ln K_{S,B} \quad (65)$$

If $g^\circ(\text{B}_{\text{aq}})$ is known (from a thermodynamic database) and $K_{S,B}$ is fitted in the adsorption modeling exercise then $g^\circ(\text{B}_{\text{ads}})$ can be calculated from Eq. (65). Alternatively, if $g^\circ(\text{B}_{\text{ads}})$ value is known from fitting then $K_{S,B}$ can be calculated.

Eqs. (64) and (65) are also valid for water, with the difference that the reference state is now the full coverage in the monolayer of adsorbed water, and the binding constant $K_{S,W}$ includes a conversion factor (55.5084) from the molal scale for $\text{H}_2\text{O}_{\text{ads}}$ to the mole-fraction scale for $\text{H}_2\text{O}_{\text{bulk}}$:



The difference between reactions Eq. (66) and Eq. (64) lies also in the fact that in dilute aqueous electrolytes, the activity of water $\{H_2O_{\text{bulk}}\}$ is constant and close to one, therefore the activity of adsorbed water $\{H_2O_{\text{ads}}\} \approx 55.5084$. As shown above (Section 4.1), this leads to “yielding” behavior of adsorbed water in competition with surface species bound much stronger to the surface, with implications for the surface activity coefficient term of H_2O_{ads} or $\equiv OH$ species.

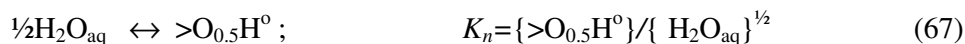
(2) If a “clean” hydroxylated surface is covered with a monolayer of physically adsorbed water forming a “surface solvent”, and the site-binding reactions occur through the displacement of molecules of this solvent, then its activity will be fixed by that of the bulk liquid water present in equilibrium, again indifferent to the amounts of water and sorbent, to its specific surface area, and to the current density of surface complexes.

We see that in both cases (1) and (2), the mole-fraction activity of surface sites or “surface solvent” $\equiv OH$ groups should be taken (almost) equal to unity. Thus, the denominator of LMA expression for reactions like the $site + B_{\text{aq}} \leftrightarrow B_{\text{ads}}$ can be written as $a_{>SOH} a_B$, where $a_{>SOH} = \text{const.}$

The elemental stoichiometry of $\equiv OH^0$ species, viewed as a “surface solvent”, must contain water, with an ambiguity whether to include the adsorbent atoms or not (e.g., $[TiO_{1.5}]OH^0$ or OH^0). To resolve this ambiguity, a cornerstone decision must be made before proceeding with the compilation of a unified thermodynamic adsorption database. The involvement of adsorbent atoms would make the standard molar properties of surface species dependent on the composition of the sorbent surface layer. Consequently, these properties would be valid only over a given mineral surface and may not be comparable even between different faces of the same mineral particle. However, it will be clearly beneficial to have the standard properties of surface species comparable between different mineral adsorbents.

Perhaps, this problem is more important for the GEM than for the LMA approach, because in the latter, the sorbent only *identifies* the site balance constraint and, thus, its stoichiometry is not relevant. Besides, for some solid sorbents (solid solutions, clay minerals, aluminosilicates, ion-exchange resins) it is difficult, if not impossible, to identify a fixed part of their stoichiometry that can be assigned to surface species.

In view of such problems, the choice to *separate* stoichiometry of the sorbent from that of surface species [18, 55] makes their standard molar properties such as g^0 and S^0 comparable between different surfaces and minerals, and consistent with that of aqueous sorbates, solids and gases. Such “definite elemental stoichiometry” monodentate surface species will be designated with a ‘>’ symbol, which simply shows that the component belongs to the surface of a sorption phase; the ‘ \equiv ’ symbol will be retained for the “generic” surface species. For compatibility with 2-pK adsorption reactions, the simplest possible stoichiometry ($O_{0.5}H^0$) of the neutral amphoteric $>O_{0.5}H^0$ functional group can be defined through the reaction:



The value of $g_{298}^0(>O_{0.5}H^0) = -128.548 \text{ kJ}\cdot\text{mol}^{-1}$ at reference temperature $T_o = 298.15 \text{ K}$ has been determined in GEM model calculations of the $>O_{0.5}H^0$ coverage on simple oxide sorbents of different specific surface areas immersed in pure water [18] by adjusting g_{298}^0 until the standard density $\Gamma_o = 2.0 \cdot 10^{-5} \text{ mol}$ of the $>O_{0.5}H^0$ species is achieved. Recalculating to $\Delta_r G$ and then to K_n gives $\Delta_r G_{n,298}^0 = -9.957 \text{ kJ}\cdot\text{mol}^{-1}$ and $\log K_n = 1.74436$, or $K_n = 55.5084$. The last value simply equals the conversion factor from the molal to mole fraction scale

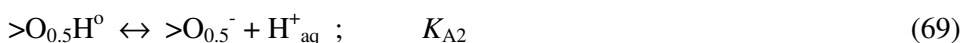
$1000/M(\text{H}_2\text{O})$, where $M(\text{H}_2\text{O}) = 18.0153 \text{ g mol}^{-1}$ is the gram-formula mass of H_2O . Hence, the equilibrium constant of reaction Eq. (67) is unity if the activity of $>\text{O}_{0.5}\text{H}^0$ is taken in the mole fraction scale. In other words, the stability of the surface “water solvent” $>\text{O}_{0.5}\text{H}^0$ is taken the same as that of the bulk liquid water.

5.3. Stoichiometry and standard Gibbs energy of 2-pK surface complexes

Two $>\text{O}_{0.5}\text{H}^0$ species can be viewed as one H_2O molecule coordinated to two primary oxygen surface sites of Γ_0 density *on any* solid (hydr)oxide surface. Further, the reaction



describes the transfer of a “surface hydronium” ($\text{O}_{0.5}\text{H}_2^+$) into the aqueous proton (H_{aq}^+). Another reaction



can be considered as a dissociation of the “surface solvent” ($\text{O}_{0.5}\text{H}^0$) into a „surface hydroxyl“ ($\text{O}_{0.5}^-$) and an aqueous proton. Both reactions correspond to the macroscopic 2-pK notation. Standard molar properties and stoichiometry of $>\text{O}_{0.5}\text{H}^0$, as such, imply no specific features of a particular mineral surface such as geometry, density, or attributed charge. Rather, the $>\text{O}_{0.5}\text{H}^0$ species is a thermodynamic entity needed to connect the standard partial molal properties of surface complexes to that of chemical elements, aqueous ions, minerals and gases. This does not mean that the chemical nature of the mineral surface is totally neglected: the molecular-specific properties can and should be assigned to stoichiometries and standard partial molar properties of the surface complexes and their Γ_C parameters, rather than to the properties of the $>\text{O}_{0.5}\text{H}^0$ groups which comprise a reference species common to all hydrated surfaces.

For instance, a mineral surface-specific $g^0(>\text{O}_{0.5}^-)$ value can be found from the common $g^0(>\text{O}_{0.5}\text{H}^0)$ and the known K_{A2} value (using $\Delta G_r^0 = -RT \ln K$), or, vice versa, K_{A2} can be calculated from $g^0(>\text{O}_{0.5}\text{H}^0)$ and known (fitted or predicted) value of $g^0(>\text{O}_{0.5}^-)$. In other words, the $g^0(>\text{O}_{0.5}\text{H}^0)$ value tells nothing specific about the surface and sites, while the $g^0(>\text{O}_{0.5}^-)$ value describes how basic the surface of a particular mineral is, and, together with the $g^0(>\text{O}_{0.5}\text{H}_2^+)$ value, determines pH_{PPZC} and the surface “amphoteric strength” $\Delta \text{p}K_A = \log_{10} K_{A1} - \log_{10} K_{A2}$ referred to the standard surface density [10].

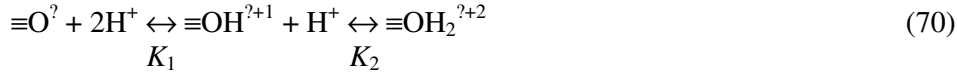
A major weakness of 2-pK SCMs is often seen in the involvement of the $\equiv\text{OH}^0$ (or $>\text{O}_{0.5}\text{H}^0$) species, activity of which is constant as long as the liquid H_2O is present in excess. This makes the LMA-fitted intrinsic constants K^{int} highly sensitive to the site density parameter Γ_C (see Eq. 43) and the chosen value of $\Delta \text{p}K_A$ (usually between 2 and 6). Note that in GEM SCMs, the $>\text{O}_{0.5}\text{H}^0$ species does not affect the fits to titration data at all and may be dropped from the model.

5.4. Determining stoichiometry and Gibbs energy of MUSIC surface species

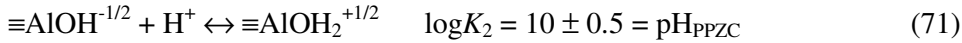
Hiemstra and Van Riemsdijk ([28], see also chapter by Van Riemsdijk and Hiemstra in this book) considered in detail the surface structure and protonation states of surface sites for several important (hydr)oxides (SiO_2 , TiO_2 , $\alpha\text{-Al}(\text{OH})_3$, $\alpha\text{-FeOOH}$, $\alpha\text{-Fe}_2\text{O}_3$) in water. Depending on the crystal structure, the cation charge, and the crystallographic plane, the surface oxygens can be singly-, doubly-, or triply- coordinated to metal atoms. The unsatisfied charge on the particular surface oxygen site can be approximated using the Pauling *bond-*

valence principle, and the density of such sites can be found from crystallographic data. The picture of surface hydroxylation is qualitatively similar to that explained above (Eq. 58): the dissociative adsorption of H₂O molecules results in acidic functional groups like ≡SiOH⁰, or amphoteric groups like ≡Al₂OH⁰ on gibbsite (001) face (unreactive within pH range 4 to 10), or basic ≡AlOH₂^{0.5} groups on gibbsite edge faces, or TiOH^{-0.33} groups, as determined in the Multi-Site Complexation (MUSIC) approach [28].

The related reactions are mostly written similar to the 1-p*K* formalism [27, 28, 72, 73], where the neutral amphoteric ≡OH⁰ group is not used. In the MUSIC approach, the surface protonation reactions have a general form



where the question mark indicates various charge attributions that depend on the mineral structure and on the coordination of surface oxygens. The difference $\Delta pK = \log K_1 - \log K_2$ for the consecutive protonation steps on all oxides is shown to be not less than 12, so large that only one protonation step can be observed in the experimental pH window [28]. Conversely, a single protonation reaction is usually sufficient for describing the pristine surface charging of an oxide surface. For instance, in the pH range 4-10, the surface protonation of **gibbsite** α -Al(OH)₃ is described [28] by:



In this model, the equilibrium constants K_1 or K_2 should not depend on the standard-state density Γ_0 because the corrections Eq. (43) apply equally to both surface complexes and divide out in LMA expressions.

Since both surface species have fractional charges, and no “surface solvent” is involved into Eq. (71), the determination of elemental stoichiometries is not as straightforward as in the 2-p*K* notation (Eq. 67). Fortunately, the Pauling bond valence concept can be used in finding the elemental stoichiometries of surface complexes on a given crystallographic site type. This is also a pre-requisite for the implementation of CD MUSIC-type SCMs in thermodynamic models without site balance constraints. In this contribution, such definition of surface complexes stoichiometries is described for the first time.

The Pauling bond valence ν expresses the mean available charge per bond as the charge z of the metal ion divided by its coordination number CN [28]:

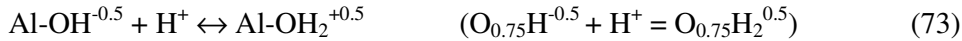
$$\nu = z/CN \quad (72)$$

In oxides, CN is usually 4 (e.g., Si⁴⁺ in SiO₂ phases) or 6 (coordination of Al³⁺ in aluminum hydroxides or clays). The reactive oxygen in Eq. (71) is singly coordinated to an aluminum atom with a bond valence of $3/6 = +1/2$. Together with the formal -2 valence of the free oxygen ion, this gives for the ≡AlO[?] species the charge -3/2, for the ≡AlOH[?] species the charge -1/2, and for the ≡AlOH₂[?] species – the charge +1/2, as shown in Eq. (71).

To find the elemental stoichiometry of a complex on surface oxygen like those considered above, the following principle can be used. The oxygen has to be “divided” into two parts: one part compensating the bond valence must be assigned back to the oxide sorbent, and another part that must be assigned to the surface complex. This operation

eliminates the charge imbalance in the solid sorbent composition, which may dramatically affect the sorbent stability at significant specific surface areas and site densities.

In our example with gibbsite surface species, the bond valence of $\frac{1}{2}$ must be compensated by $\frac{1}{2} / 2 = 0.25$ oxygens. Indeed, 0.25O per each of 6 bonds per Al ion gives $0.25 \cdot 6 = 1.5$ oxygens, or the oxide stoichiometry $\text{AlO}_{1.5}$ or Al_2O_3 , hence, this operation does not introduce any charge imbalance into the solid. The rest, 0.75 oxygens, has the formal charge of $-2 + 0.25 \cdot 2 = -1.5$ and can stay in place of the $\equiv\text{AlO}^{-1.5}$ moiety. Hence, the elemental stoichiometry of the $\equiv\text{AlOH}^{-1/2}$ surface species should be written as $\text{O}_{0.75}\text{H}^{-0.5}$, and that of $\equiv\text{AlOH}_2^{+1/2}$ species as $\text{O}_{0.75}\text{H}_2^{0.5}$. The whole protonation reaction on gibbsite edge surface takes the form

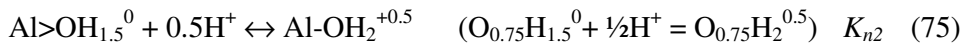
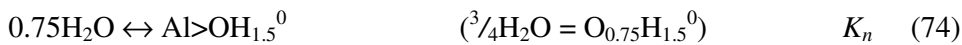
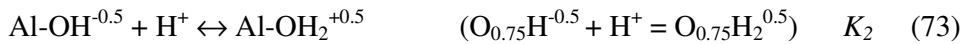


where “Al-“ symbolizes a single bond stemming from the Al^{III} atom which, however, itself is not included into the stoichiometry of surface complexes. In the reaction notation (left), fractional coefficients for oxygen are omitted for brevity. The elemental reaction stoichiometry is shown in parentheses on the right side.

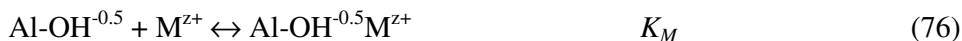
The determination of standard molar Gibbs energies g_{298}° for $\text{Al-OH}^{-0.5}$ and $\text{Al-OH}_2^{+0.5}$ surface species in Eq. (73) is also less straightforward than that for the 2-pK surface species because the reaction (73) fixes only the *difference* $\Delta_r G^\circ = g^\circ(\text{Al-OH}_2^{+0.5}) - g^\circ(\text{Al-OH}^{-0.5}) = -RT \ln K_2$ ($g^\circ(\text{H}^+) = 0$ by convention). As long as this difference remains the same, the standard molal Gibbs energies of both surface complexes can be made simultaneously more positive or more negative.

Again, this plays no role in site balance based LMA SCMs, but is an important point in GEM SCMs without site balance constraints. From general thermodynamic reasoning, one can deduce that the surface protonation according to reaction (73) as a function of aqueous pH will be the steeper the more negative *both* Gibbs energies $g^\circ(\text{Al-OH}_2^{+0.5})$ and $g^\circ(\text{Al-OH}^{-0.5})$ are, although any such curve goes through the same pH_{PPZC} (and corresponds to the same K_2 value).

Hence, *both* standard Gibbs energies should be adjusted at the same time in GEM SCM against potentiometric titration data at low ionic strength using an appropriate EDL model and, for all surface species competing for sites of the same type, the competitive Langmuir SACT (Eq. 32) with the site density Γ_C value found from crystallographic data. Results can be conveniently represented using equilibrium constants of the reactions:



The electrolyte adsorption (i.e. formation of surface ion-pairs of cations M and anions L of single-ion electrolyte ML) on the gibbsite edge surface is usually described via the reactions



Hiemstra et al. [74] have found $\log_{10}K_L = 0.1$ (at capacitance density $C_1 = 0.9 \pm 0.1 \text{ F}\cdot\text{m}^{-2}$) and supported the suggestion of Lützenkirchen et al. [75] to assume the symmetric electrolyte adsorption, i.e. $K_M = K_L$ for (hydr)oxide surfaces with high pH_{PZC} such as gibbsite or goethite.

Reaction (74) is assumed to have the same properties ($\log_{10}K_n = 1.74436$, $\Delta_{r,n}H^\circ_T \equiv 0$, and $\Delta_{r,n}Cp^\circ_T = 0$) as Eq. (67) of formation of the fictive “surface solvent” from the bulk water. This yields $g^\circ_{298}(\text{Al>OH}_{1.5}^0) = -187.844 \text{ kJ}\cdot\text{mol}^{-1}$ for the elemental stoichiometry $(\text{H}_2\text{O})_{0.75}$. Reaction K_{n2} (Eq. 75) connects this value with that of the fully protonated surface complex $\text{Al-OH}_2^{+0.5}$, which, in turn, is linked to the g°_{298} value of the $\text{Al-OH}^{-0.5}$ surface complex via the reaction K_2 (Eq. 73) and to g°_{298} values of outer-sphere complexes $\text{Al-OH}^{-0.5}\text{M}^{z+}$ and $\text{Al-OH}_2^{+0.5}\text{L}^{z-}$ through reactions (76) and (77), respectively.

So, in order to find the whole set of standard Gibbs energies of surface complexes, one has to take a guess value of K_{n2} (e.g. 100); calculate g°_{298} values for all four species using thermodynamic data for aqueous ions [76]; put species stoichiometries with g°_{298} values and other parameters into the SCM; and adjust g°_{298} *simultaneously* using the same g° increment in modeling titration data.

Determination of $\log_{10}K_{n2}$ value which sets up the “strength” of both gibbsite edge surface species $\text{Al-OH}^{-0.5}$ and $\text{Al-OH}_2^{+0.5}$ has been performed as outlined above using the basic Stern (BS) SCM in the GEMS-PSI code (available for downloading from <http://les.web.psi.ch/Software/GEMS-PSI/>) with thermodynamic data for aqueous species and gibbsite $\text{Al}(\text{OH})_3$ from the GEMS version of the Nagra-PSI data base [77].

The adjustment of g°_{298} values of surface complexes has been done in fitting potentiometric titration data for 30 g/L gibbsite GL1 in 0.1 and 0.005 M NaNO_3 solutions [74] with edge specific surface $A_{\text{edge}} = 20.3 \text{ m}^2\cdot\text{g}^{-1}$ and the recommended capacitance density parameter $C_1 = 0.9 \text{ F}\cdot\text{m}^{-2}$. In the GEM SCM, competitive Langmuir SACT corrections (Eq. 32) were calculated together with the BS electrostatic corrections and the aqueous activity coefficients. The latter were found from the Debye-Huckel equation with the common ion size parameter $a^\circ = 3.72 \text{ \AA}$ and the common “salting-out” parameter $b_\gamma = 0.064$.

As seen on Fig. 6, quite good fits at both NaNO_3 concentrations have been obtained at g°_{298} values that correspond to a $\log_{10}K_{n2} = 5.3$ in reaction Eq. (75). Note that this value is consistent only with the chosen inner capacitance $C_1 = 0.9 \text{ F}\cdot\text{m}^{-2}$ because they were found to be inter-dependent. The numerical value of K_{n2} refers to the standard-state density value $\Gamma_0 = 2\cdot 10^{-5} \text{ mol}\cdot\text{m}^{-2}$ just like for any other direct binding reaction because of the constant activity of the (fictive) $\text{Al>OH}_{1.5}^0$ species. A thus established thermodynamic data set for gibbsite edge surface is provided in Table 2. Standard g°_{298} values for surface ion pairs other than for Na^+ and NO_3^- can be computed from reactions (68), (67) and data for aqueous ions [76] using the same K_M and K_L .

As seen on Fig. 6, the BS MUSIC model for gibbsite can be successfully reproduced without the site balance constraint which, in the GEM variant, had been replaced by Langmuir competitive SACT corrections (Eq. 32) added to usual BS electrostatic terms for all four surface complexes.

Unlike the 2-pK SCMs, this model behaves non-ideally in the whole pH interval (values of $\chi_{s,L}$ vary from 9.1 at $\text{pH}=4$ to 7.5 at $\text{pH}=12$). This is a consequence of a rather large value of $K_{n2} = 199'526$ found in this modeling exercise. The surface speciation seen on Fig. 6 is quite similar to that produced in “standard” site balance based LMA MUSIC SCMs.

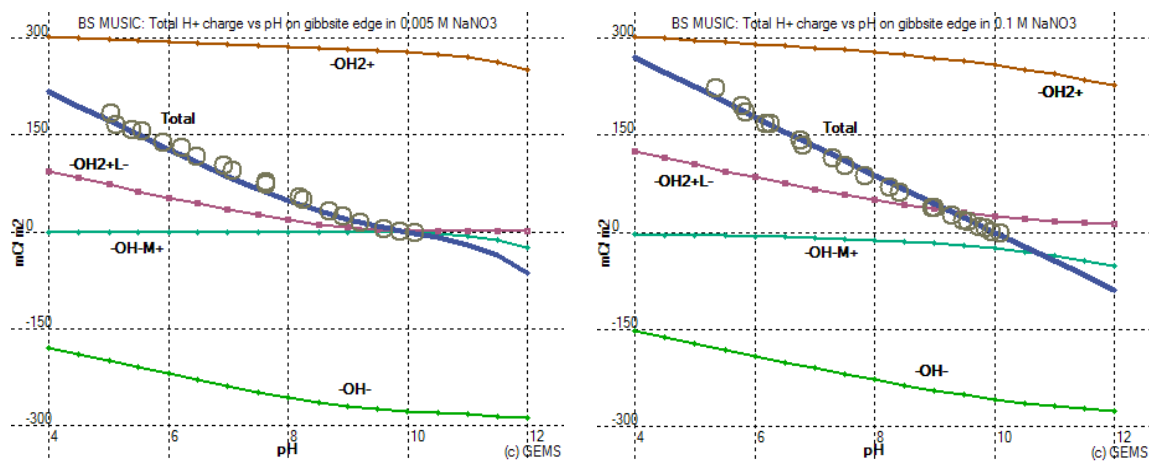


Fig. 6. Charging behavior of gibbsite, modeled at 25 °C using GEM BS SCM (data Table 2) at 0.005 M NaNO₃ (left) and 0.1 M NaNO₃ (right). Scattered circles – experimental data (Fig. 6 in [74]). Screenshots from a series of GEMS-PSI equilibria calculations (small dots on the lines indicate particular equilibria computed with a pH step of 0.5). Proton surface charge σ_H in the zero plane of the gibbsite edge is expressed in mC·m⁻². Total σ_H and its contributions from individual surface complexes were calculated as given by (Eq. 30 in [78]).

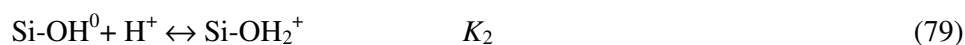
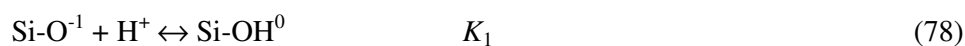
Table 2

Thermodynamic data for GEM (MUSIC) BS model of protonation on gibbsite edges

Species	Stoichiometry	Reaction Eq.	$\log_{10}K$	g_{298}° kJ·mol ⁻¹	Label on Fig.6
Al-O _{0.75} H ₂ ^{+0.5}	O _{0.75} H ₂ ^{+0.5}	(75)	5.3 ^A	-218.10	-OH2+
Al-O _{0.75} H ^{-0.5}	O _{0.75} H ^{-0.5}	(73)	10.0	-161.02	-OH-
Al-O _{0.75} H ₂ ^{+0.5} L ^{z-}	O _{0.75} H ₂ L ^{-z+0.5}	(77)	0.1	-329.57*	-OH2+L-
Al-O _{0.75} H ^{-0.5} M ^{z+}	O _{0.75} HM ^{+z-0.5}	(76)	0.1	-423.47*	-OH-M+

^A This work; * for NaNO₃ electrolyte ($g_{298}^{\circ}(\text{Na}^+) = -261.88$; $g_{298}^{\circ}(\text{NO}_3^-) = -110.905$ kJ·mol⁻¹ [76]), assuming symmetric electrolyte adsorption [27]. Site density parameter $N_C = 8.15$ nm⁻² [74] ($\Gamma_C = 1.353 \cdot 10^{-5}$ mol·m⁻²), capacitance density $C_1 = 0.9$ F·m⁻²; specific surface area of gibbsite edges must be known in SCM applications.

The outlined method for deriving stoichiometry and standard molal Gibbs energy of surface complexes using the Pauling bond valences can be applied to other oxides. On SiO₂ surfaces (cristobalite, quartz, silica), mainly the singly coordinated Si-O- group is proton reactive. This species has the formal charge of -1 v.u. because the Si-O bond valence equals unity (Si⁴⁺ ions have CN = 4). The protonation process is then described via reactions



([28], see also chapter by Mielczarski and Pokrovsky in this book) which have the same form as the (reversed) 2-pK reactions (Eqs. 68, 69). MUSIC-predicted values are $\log_{10}K_1=7.7$ and $\log_{10}K_2=-4.0$ [79] with $\text{pH}_{\text{PPZC}} \approx 2$ and $\Delta\text{p}K \approx 12$. The second protonated species is non-existent at $\text{pH} > 2$. The elemental stoichiometries of silica surface species should contain $\frac{1}{2}\text{O}$ because 1 v.u. of charge and thus $\frac{1}{2}\text{O}$ is taken by one of four silicon bonds. This results in $\text{O}_{0.5}^-$, $\text{O}_{0.5}\text{H}^0$ and $\text{O}_{0.5}\text{H}_2^+$ stoichiometries. The contribution of the neutral species Si-OH^0 to surface charging behavior cannot be seen from potentiometric titration data. Hence, this species can be considered as a “surface solvent”, and its properties taken the same as those of $>\text{O}_{0.5}\text{H}^0$ group in 2-pK models (Eq. 58).

Standard molal Gibbs energies of deprotonated and protonated species can then be calculated through equilibrium constants K_1 and K_2 . Note that in this case, both K_1 and K_2 are sensitive to the standard-state density Γ_0 choice (see Eq. 43), so their predicted values given above may correspond to intrinsic constants K^{int} referred to the site density Γ_C which is rather uncertain ($4 < N_C < 7 \text{ nm}^{-2}$). Structural values for SiO_2 surfaces are ca. $\Gamma_C = 8 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ ($N_C = 4.8 \text{ nm}^{-2}$); the conversion to $\Gamma_0 = 20 \text{ mol} \cdot \text{m}^{-2}$ may thus increase $K_1^{\text{int}} = 7.7$ to $\log_{10}K_1 = 8.1$.

The electrolyte adsorption (formation of outer-sphere surface complexes) on SiO_2 surfaces is thought to be rather weak. It is described via the reactions



of which the second one may play a role only at extremely low pH. For equilibrium constants K_M and K_L , the values $\log_{10}K = -1.5$ or less are recommended [74]; these can now be easily converted into g_{298}^0 values for both outer-sphere electrolyte surface complexes (Table 3).

Table 3

Thermodynamic data for GEM (MUSIC) model of deprotonation on SiO_2 surfaces

Species	Stoichiometry	Reaction Eq.	$\log_{10}K$ ($\log_{10}K^{\text{int}}$)	g_{298}^0 , $\text{kJ} \cdot \text{mol}^{-1}$
Si-OH^0	$\text{O}_{0.5}\text{H}^0$	(67)	1.74436	-128.55
Si-O^-	$\text{O}_{0.5}^-$	(78)	8.1 (7.7)	-82.31
Si-OH_2^+	$\text{O}_{0.5}\text{H}_2^+$	(79)	-4.4* (-4.0)	-103.43
$\text{Si-O}^-\text{M}^{z+}$	$\text{O}_{0.5}\text{M}^{+z-1}$	(80)	-1.5	-335.63**
$\text{Si-OH}_2^+\text{L}^{z-}$	$\text{O}_{0.5}\text{H}_2\text{L}^{-z+1}$	(81)	-1.5*	-226.16**

Intrinsic constants K^{int} from [79], converted from $\Gamma_C = 7.97 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ ($N_C = 4.8 \text{ nm}^{-2}$) to Γ_0 into equilibrium constants K using Eq. (47); symmetric adsorption of electrolyte assumed. *Insignificant species at $\text{pH} > 3$; **Example values for NaCl electrolyte, calculated using $g_{298}^0(\text{Na}^+) = -261.88$; $g_{298}^0(\text{Cl}) = -131.29 \text{ kJ} \cdot \text{mol}^{-1}$ [76]. Site density parameter $N_C = 4.8 \text{ nm}^{-2}$.