Part 5. Calculation of Coulombic corrections and activity coefficients for surface species of sorption phases in built-in functions of GEM-Selektor code

The GEM approach to surface complexation models, GEM SCM [Kulik, 2000; 2002a,b], treats the multi-site-surface adsorption generally in the same way and together with the solid solutions, gases, and aqueous electrolyte in the chemical elemental stoichiometry, directly using the standard molar thermodynamic properties of surface complexes.

1. Sorption phase concept, standard and reference states of surface species

A sorption phase combines *a mineral sorbent* (1) having a prescribed *specific surface area* $A_{a,v}$ ($m^2 \cdot g^{-1}$) (2), covered with *a monolayer of primary neutral amphoteric surface functional groups* ("surface solvent") (3), part of which on different surface types (patches) (4) reacts with aqueous species forming *surface complexes* (5).

The standard state of a surface species defines a unique combination of properties (1) to (5) in a way compatible with standard states chosen for minerals, gases, water-solvent and aqueous species. This is possible only if a unique *reference site density* Γ_o value at standard state is fixed for all mineral-water interfaces, as in the following definition:

The standard state of a surface species is when 1 *mole of it is bound at reference density* Γ_o *on all the surface of* 1 *mole of the sorbent suspended in* 1 *kg of water-solvent at* $P_r=1$ *bar and defined T, in absence of external fields and at zero surface potential* $\Psi=0$.

A proposed value $\Gamma_o = 2 \cdot 10^{-5}$ mol·m^{-2} ≈ 12.05 sites·nm^{-2} roughly corresponds to the density of H_2O molecules in a surface monolayer, thus representing a realistic maximal density of monodentate surface complexes. This choice is practical and is similar to the inclusion of 1 kg (55.5084 mol) of H_2O solvent into the standard state of aqueous species.

The *reference state* of $\equiv OH^o$ functional group ("surface solvent") should occur when all such groups *are free* (non-reacted) and occupy the sorbent surface in a monolayer of reference density Γ_o, e.g. 1 mol of $\equiv OH^o$ groups on a sorbent with reference total surface area $A_o = 1/\Gamma_o = 5 \cdot 10^5$ m^2·mol^{-1} per 1 kg of H_2O. The reference state of a *j*-th surface complex (i.e. reacted $\equiv OH^o$ functional group) then occurs at a hypothetical unimolal concentration and *infinitely low surface density* Γ_o (mol·m^{-2}). These two reference states are reciprocal to the same extent as those used for the water-solvent and solutes in the aqueous electrolyte phase, respectively.

Upon the "infinite dilution" of aqueous sorbates, reference states for surface- and aqueous species and solvents are correctly approached. The definitions of standard and reference states in GEM SCMs are conceptually related to the amphoteric (hydr)oxide surfaces. However, a reasonable choice of elemental stoichiometry of the "surface solvent", *without* including the sorbent stoichiometry part, makes this thermodynamic treatment applicable to other, non-oxide or non-amphoteric surfaces (i.e. carbonates, sulfides, permanent-charge siloxane planes of clay particles or micas), as long as the surface complexation is thought to occur within a monolayer of the surface-coordinated or physically adsorbed water molecules.

The (solid) sorbent can be either a mineral or a solid solution, with end-members taken at the usual "pure substance" standard state. The only difference is that the stability of (particulate) solid having a significant specific surface area $A_{\alpha,v}$ will be affected by a surface free energy term $\Delta G_{j,s} = \frac{2}{3} k_\alpha \sigma_{j,v} M_{\alpha,v} A_{\alpha,v}$, where $M_{\alpha,v}$ is the molar mass and $\sigma_{j,v}$ is the specific Gibbs surface energy of the pure mineral (end-member) in water. The dimensionless factor k_α can be used to describe the effect of shape and size distribution of particles ($k_\alpha > 0$) or pores ($k_\alpha < 0$).

Thus, the chemical potential of the j-th sorbent (end-member) is approximated in the GEM approach as

$$\upsilon_j = \frac{g_{j,v}}{RT} + \frac{\Delta G_{j,s}}{RT} + \ln\frac{x_j}{X_a} + \ln\gamma_j + \Theta_{\alpha,v}; \quad j \in l_{\alpha,v}, \alpha \in \Phi; \qquad (5\text{-}1),$$

where $g_{j,v}$ is the molar apparent Gibbs energy function at T,P of interest, x_j is mole quantity, X_a is total mole amount of the sorption phase, γ_j is the activity coefficient, and $\Theta_{\alpha,v}$ is the asymmetry term (zero in absence of surface species, see below).

2. Surface types (patches), density parameters, and chemical potentials

Now, description of activities and (electro)chemical potentials of the surface-bound species of a multi-site-surface sorption phase becomes possible at any state of interest. It can be shown that concentration of a surface species expressed as a *surface density (mole) fraction* Γ_j / Γ_o is invariant to the mole quantity $X_{\alpha,v}$ and specific surface area $A_{\alpha,v}$ of the sorbent. Using Γ_j / Γ_o concentration scale, the activity of j-th surface species (at Ψ=0) can be expressed as:

$$a_j = \frac{\Gamma_j}{\Gamma_o}\Xi_j = \frac{A^o_{\alpha,v} x_j}{\phi_{\alpha,t} A_{\alpha,v} X_{\alpha,v}}\Xi_j \qquad (5\text{-}2),$$

where the “v” subscript denotes a “volume” part of the α-th sorption phase (i.e., the sorbent); $A^o_{\alpha,v} = 1/(M_{\alpha,v}\Gamma_o)$ (in $m^2 \cdot g^{-1}$) is the reference specific surface area at standard-state; $M_{\alpha,v}$ is the molar mass of the sorbent; x_j is a number of moles of j-th surface species; and $\phi_{\alpha,t}$ is a fraction of total specific surface area $A_{\alpha,v}$ assigned to t-th surface type; thus, several different surface “patches” (up to six in GEMS code) can be considered on one sorbent. $\Xi_j = f(x_j, \Gamma_{max})$ stands for a *surface activity term* (SAT) - a special “concentration correction” term that replaces the balance constraint on the maximum number of surface sites available for the j-th species. SAT may also incorporate the activity coefficients responsible for any non-thermodynamic (lateral) interactions between surface species (see below).

The right-hand side of eqn (5-2) connects the surface density fraction Γ_j / Γ_o to molar quantities of the sorbent and the surface species. It can be derived according to the equations:

$$\frac{\Gamma_j}{\Gamma_o} = \frac{x_j}{\chi^o_{\alpha,t}}; \quad \chi^o_{\alpha,t} = \phi_{\alpha,t} X_{\alpha,v} M_{\alpha,v} A_{\alpha,v} \Gamma_o; \quad \Gamma_o = \frac{1}{M_{\alpha,v} A^o_{\alpha,v}} \qquad (5\text{-}3)$$

where $\chi^o_{\alpha,t}$ defines an expected mole quantity of surface species at reference density on t-th surface type on α-th sorbent. As seen from eqn (5-3), usage of the “reference specific surface area” $A^o_{\alpha,v}$ is equivalent to eliminating the molar mass of the sorbent from eqn (5-2). Substituting eqn (5-2) into the definition of electrochemical potential, $\mu = \mu^o + \ln a + C_F$ (C_F is the Coulombic term), one obtains an (electro)chemical potential of a j-th surface species:

$$\upsilon_j = \frac{g^o_{j,T}}{RT} + \ln 55.5084 + \ln\frac{A^o_{\alpha,v}}{\phi_{\alpha,t} A_{\alpha,v}} + \ln\frac{x_j}{X_{\alpha,v}} + \ln\Xi_j + \frac{F}{RT} z_j \Psi_{\alpha,t} \qquad (5\text{-}4),$$

where z_j is the effective formula charge, F = 96485 $C \cdot mol^{-1}$ is the Faraday’s constant, $\Psi_{\alpha,t}$ is an electrostatic potential on t-th surface type (at EDL plane), R= 8.3145 $J \cdot K^{-1} \cdot mol^{-1}$ is the universal gas constant, ln(55.5084) converts from the molality concentration units, in which $g^o_{j,T}$

is taken, and the asymmetry term is omitted for brevity. The $g^{o}_{j,T}$ stands for the standard partial molal Gibbs energy function of *j*-th surface species at temperature *T* of interest. The sum of all terms on the right-hand side of eqn (5-4) but the first one operationally defines activity of a surface species as a difference of chemical potentials: $a_j = \mu_j - \mu^{o}_{j}$.

Eqn (5-4), central in GEM SCM implementations, contains all necessary conversions from the state of interest to standard/reference states, and fully reflects the “interfacial” nature of surface species. This equation is also helpful in determining equilibrium constants of surface species from their G^{o}_{298} values for usage in the LMA-based speciation algorithms.

More precisely, the following approximation of (electro)chemical potential of a surface species is used in the GEM-Selektor code:

$$\upsilon_j = c_j + \ln\frac{x_j}{X_\alpha} - \ln\frac{X_{\alpha,v}}{X_\alpha} + \Theta_{\alpha,s} \quad \text{where}$$

$$c_j = \frac{g_{j,T,P}}{RT} + 4.016534 + \ln\frac{A^{o}_{\alpha,v}}{\varphi_{\alpha,t}A_{\alpha,v}} + \ln\Xi_j + \frac{F}{RT}z_j\Psi_{\alpha,t}, \quad j \in l_{\alpha,s} \tag{5-5}$$

where $l_{\alpha,s}$ is a subset of indices of surface species on α-th sorption phase, and $\Theta_{\alpha,s}$ is an *asymmetry term* common to all surface species:

$$\Theta_{\alpha,s} = 1 - \frac{X_{\alpha,v}}{X_\alpha} - \frac{\theta_0}{1+\theta_0}, \quad \text{where} \quad \theta_0 = A_{\alpha,v}M_{\alpha,v}\Gamma_o \qquad (5\text{-}6).$$

The respective asymmetry term for the sorbent (see eqn 5-1) is

$$\Theta_{\alpha,v} = 2 - \frac{X_\alpha}{X_{\alpha,v}} - \frac{X_{\alpha,v}}{X_\alpha} + \theta_0 - \frac{\theta_0}{1+\theta_0} \qquad (5\text{-}7).$$

Both asymmetry correction terms help obtaining a feasible initial approximation and an efficient numerical convergence of the GEM IPM non-linear minimization algorithm. They tend to zeros when the specific surface area (and thus θ_0) tends to zero. The SAT term $\ln\Xi_j$ (forming the activity coefficient part together with the Coulombic term $\frac{F}{RT}z_j\Psi_{\alpha,t}$, see Section 3) will be described below (Section 4).

3. Surface complexation models and Coulombic corrections implemented in GEMS

The GEM SCM approach does not use mass balance constraints for total mole amounts of surface sites, hence, the stoichiometric formulae of surface species can include only chemical elements and charge, similar to formulae of aqueous species or gases [Kulik, 2002a]. An ambiguity there consists in whether or not to include atoms of the solid sorbent in the formulae.

3.1. Stoichiometry and thermodynamic properties of surface species

Classic 2pK_A SCMs – triple layer model (TLM), double layer model (DLM), or constant capacitance model (CCM) – assume that oxide surfaces expose *neutral amphoteric* $\equiv$OH^{o} *functional groups* which can react with aqueous species via (de)protonation, exchange with anions, or binding of aqueous cations into the outer- or inner-sphere surface complexes [see overviews by Stumm, 1992; Lützenkirchen, 2002]. In this framework, the standard partial molal properties (G^{o}_{298}, H^{o}_{298}, S^{o}_{298}, and Cp_{298}) of a surface complex can be calculated as usual via the respective adsorption reaction and its thermodynamic equilibrium constant K, if the standard-state molal properties and the elemental stoichiometry of the $\equiv OH^o$ group are provided.

Elemental stoichiometry of the $\equiv OH^o$ species viewed as "surface solvent" must contain water, with an ambiguity whether to include the sorbent atoms or not (e.g., $[TiO_{1.5}]OH^o$ versus OH^o). In GEM SCMs, the sorbent atoms are excluded, which makes the standard partial molal properties of surface species comparable between different surfaces and minerals, as well as consistent with that of aqueous sorbates, solids and gases. Such "definite elemental stoichiometry" of (monodentate) surface species will be designated with '>' symbol, which simply shows that the species belongs to the surface of a sorption phase; the '≡' symbol will be retained for the "generic" LMA surface-bound species. The $O_{0.5}H^o$ formula provides the simplest stoichiometry of the $>O_{0.5}H^o$ functional group [Kulik, 2000; 2002a,b]:

$$0.5H_2O_{aq} = >O_{0.5}H^o\ ; \qquad K_n \qquad (5\text{-}8).$$

From the value of $G^o_{298}(>O_{0.5}H^o) = -128.548$ kJ·mol^{-1} (in molal scale), it follows that $\Delta G^o_{n,298} = -9.957$ kJ·mol^{-1}, and $\log K_n = 1.74436$ at any temperature. Two $>O_{0.5}H^o$ species can be viewed as one H_2O molecule kept at two primary sites of reference Γ_o density *on any* solid (hydr)oxide surface. Further, the first and second deprotonation reactions

$$>O_{0.5}H_2^+ = >O_{0.5}H^o + H^+_{aq}\ ; \quad K_{A1} \qquad (5\text{-}9)$$

$$>O_{0.5}H^o = >O_{0.5}^- + H^+_{aq}\ ; \quad K_{A2} \qquad (5\text{-}10)$$

describe the pristine surface proton charge made of two surface species: a "surface proton" $O_{0.5}H_2^+$ and a „surface hydroxyl" ($O_{0.5}^-$). Values of K_{A1} and K_{A2} can be found from values of $G^o(>O_{0.5}H_2^+)$ and $G^o(>O_{0.5}^-)$ directly fitted in GEM modelling against the potentiometric titration data (also at different temperatures). Alternatively, these equilibrium constants can be obtained by converting the LMA-fitted intrinsic surface deprotonation constants K_{A1}^{int} and K_{A2}^{int} at known site density parameter Γ_C using an approximate formula:

$$\log K_j = \log K_{C,j}^{\mathrm{int}} + sign\ \log(\Gamma_C / \Gamma^o) \qquad (5\text{-}11),$$

where $sign$ = - for reactions like (5-9) with the $>O_{0.5}H^o$ species on the right side, and $sign$ = + for reactions like (5-10). Such a conversion, however, is not necessary for any reaction between two (monodentate) surface complexes no involving the "surface solvent" species $>O_{0.5}H^o$. For instance, summation of reactions (5-9) and (5-10) results in another reaction

$$>O_{0.5}H_2^+ = >O_{0.5}^- + 2H^+_{aq}\ , \quad \log K_{A12} = \log K_{A1} + \log K_{A2} = -2pH_{PPZC} \qquad (5\text{-}12).$$

This reaction determines a measurable property of mineral-water interfaces – the pH of pristine point of zero charge – and, as expected, its equilibrium constant is independent of the site density parameter. For that reason, reactions such as (5-12) are used in the 1pK surface complexation models [cf. Lutzenkirchen, 2002]. Contrary to that, subtracting reaction (5-10) from (5-9) produces another parameter ΔpK_A

$$>O_{0.5}H_2^+ + >O_{0.5}^- = 2>O_{0.5}H^o, \quad \log K_{A\Delta} = \log K_{A1} - \log K_{A2} = \Delta pK_A \qquad (5\text{-}13),$$

which determines the strength of both constants K_{A1} and K_{A2} in 2pK SCM. The intrinsic $\Delta pK_A^{\mathrm{int}}$ parameter depends on the chosen site density parameter Γ_C:

$$\Delta pK_A = \Delta pK_A^{\mathrm{int}} - 2\log(\Gamma_C / \Gamma^o) \qquad (5\text{-}14).$$

Clearly, the pristine surface acidity can be described in LMA SCMs using two parameters: either pK_{A1} and pK_{A2} or pH_{PPZC} and ΔpK_A, because they can be inter-converted as shown above. However, in GEM SCMs, both ways are essentially equivalent (and are also similar to

1pK SCMs) because only elemental stoichiometries and partial molal G^o values of surface complexes are used according to eqn (5-5).

Standard molal properties and stoichiometry of the $>O_{0.5}H^o$ species, as such, imply no specific features of a particular mineral surface such as geometry, density, number and charge of the broken bonds, etc. Rather, the $>O_{0.5}H^o$ species should be viewed as a conventional 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 imply that chemical nature of the mineral surface is neglected: in GEM SCMs, the chemical specificity is assigned to stoichiometries and standard partial molal properties of surface complexes and, optionally, to their maximum site density Γ_{max} parameters.

Temperature corrections for pH_{PPZC} and pristine surface species up to 300 °C are relatively easy to do using only values of pH_{PPZC}, K_{A1} and K_{A2} at reference temperature T_r (25 °C) and one- or three-term extrapolations of reactions (5-8) to (5-10) and (5-12) [Kulik, 2000]:

$$\log K_{n,T} = 1.74436;\ \Delta S^o_T = \Delta S^o_{Tr} = 33.395 \text{ J K}^{-1} \text{mol}^{-1};\ \Delta H^o_T = 0;\ \Delta Cp_T = 0 \qquad (5\text{-}15),$$

$$\text{pH}_{PPZC,T} = -29.134 + \frac{T_r}{T}\left(\text{pH}_{PPZC,T_r} + 3.2385\right) + 4.545 \ln T \qquad (5\text{-}16),$$

$$\log K_{A1,T} = \frac{T_r}{T} \log K_{A1,T_r};\quad \Delta S^o_{A1,T} = 0;\quad \Delta Cp_{A1,T} = 0 \qquad (5\text{-}17),$$

$$\log K_{A2,T} = 58.268 + \frac{T_r}{T}\left(-\log K_{A2,T_r} - 6.477\right) - 9.09 \ln T \qquad (5\text{-}18).$$

Note that the last equation is misprinted in [Kulik, 2000] and corrected in [Kulik, 2001]. These extrapolations are implemented using ReacDC format of GEMS code (details in the document **`T-corrections-Reac.pdf`**). However, it is still difficult to predict temperature corrections for adsorbed cations and anions because the experimental information on hydrothermal adsorption is still very scarce.

Generic adsorbed surface species (inner- and outer-sphere). Advanced electrostatic SCMs that use the Stern-Graham EDL concept provide an account for adsorption of electrolyte ions involved in the formation of proton charge on oxide-water interfaces and the influence of electrolyte concentration on surface charge. This is done by introducing outer-sphere surface complexes of electrolyte cations and anions, for instance, in TLM for NaCl electrolyte:

$$>O_{0.5}H_2^+Cl^- = >O_{0.5}H^0 + H^+_{aq} + Cl^-_{aq}, \qquad \log K_{Cl} \qquad (5\text{-}19),$$

$$>O_{0.5}H^0 + Na^+_{aq} = >O_{0.5}^-Na^+ + H^+_{aq}, \qquad \log K_{Na} \qquad (5\text{-}20).$$

Elemental stoichiometries of such outer-sphere surface complexes in GEM SCMs will be $O_{0.5}H_2Cl^0$ and $O_{0.5}Na^0$, respectively, i.e. both species would behave analogous to HCl^0 and $NaOH^0$ species in the total mass balance. The writing like $>O_{0.5}^-Na^+$ in above reactions indicates that the complex will influence charge density separately on zero EDL plane (sorbent surface) and (with charge of opposite sign) on the beta plane (at the distance of closest approach of background electrolyte ions). This creates some implementation difficulties because the charge used for the Coulombic correction is no more the same as the formula charge. Such difficulties prevented so far the GEM implementation of the most advanced "Charge Distribution" CD MUSIC SCM, where the fractional charges attributed to different EDL planes can vary between the like-stoichiometry surface species [details in Lutzenkirchen, 2002]. The CD MUSIC model will likely be implemented in future versions of GEM-Selektor.

The chemically specific binding of (trace) aqueous metal ions M and ligands L to amphoteric surface groups on hydroxylated surfaces is described in SCMs via reactions of the following general form [Sposito, 1984]:

$$a(\equiv OH^o) + pM^{m+} + +qL^{l-} + xH^+ + yOH^- \Leftrightarrow (\equiv O)_a M_p (OH)_y H_x L_q{}^{\delta} + aH^+ \qquad (5\text{-}21),$$

$$b(\equiv OH^o) + qL^{l-} + xH^+ \Leftrightarrow (\equiv)_b H_x L_q{}^{\zeta} + bOH^-, \qquad (5\text{-}22),$$

where $\delta = pm + x - a - ql - y$ and $\zeta = x + b - ql$ are valences of the surface complexes formed. Reaction (5-21) can be interpreted as an exchange of the proton in the $\equiv OH^o$ group(s) by a metal ion or complex, whereas the reaction (5-22) implies an exchange of the whole $\equiv OH^o$ group(s) by a protonated ligand to form an *a*- or *b*-dentate surface species. In GEM SCMs, the elemental stoichiometries of such species would become $(O_{0.5})_a M_p (OH)_y H_x L_q{}^{\delta}$ and $H_{b+x} L_q{}^{\zeta}$, respectively. Taking into account eqn (5-5), one can see that the "dentateness" plays in GEM SCMs no role at low densities of surface species (i.e. close to reference state) and it should be taken into account only in SAT (surface activity terms) at high surface loading.

In advanced electrostatic models (TLM, BSM), a surface species can be considered as *inner-sphere* or *outer-sphere*, in which cases different Coulombic terms apply. In simple models (NEM, DLM, CCM) this distinction plays no role, and all surface species can be taken as "inner-sphere", i.e. located directly on the sorbent surface (zero) plane, contributing to the charge density with their formula charges.

In addition to reactions (5-21) and (5-22), the surface ion exchange (on permanent-charge siloxane surfaces of clay minerals) can be considered in SCMs using reactions like

$$qX\text{-}M1^{m1+} + M2^{m2+} = (X\text{-})_q M2^{m2+} + qM1^{m1+} \qquad (5\text{-}23) \text{ or}$$

$$X\text{-}M1^{m1+} + pM2^{m2+} = X\text{-}M2_p^{m1+} + M1^{m1+} \qquad (5\text{-}24),$$

where $q = m2/m1$, $p = m1/m2$, and X- denotes a (negative) permanent-charge binding site. The corresponding direct binding reactions release no protons or hydroxyls and can be written in several forms:

$$M^{m+}{}_{aq} + mX\text{-} = (X\text{-})_m M^{m+} \qquad (5\text{-}25),$$

$$\tfrac{1}{m} M^{m+}{}_{aq} + X\text{-} = X\text{-}M^{+}_{1/m} \qquad (5\text{-}26),$$

$$M^{m+}{}_{aq} = M^{m+}{}_{surface} \qquad (5\text{-}27),$$

$$M^{m+}{}_{aq} + qH_2O^o{}_{surface} = M^{m+}{}_{surface} + qH_2O \qquad (5\text{-}28).$$

The resulting surface species can be treated as outer-sphere (the charge contributes to beta-plane) or inner-sphere (charge is assigned to zero plane), depending on the electrostatic model of choice. In GEM SCM implementation, stoichiometry of such surface species is the same as that of the aqueous counterpart; usage of reaction (5-27) seems to be preferable [Kulik, unpublished report], because no additional mass balance is provided for X- surface sites; instead, permanent surface charge density is an input parameter for each surface type. In addition, SAT corrections may apply based on this site density.

3.2. Non-electrostatic model, NEM

Reactions like those shown above apply also for the non-electrostatic (NEM) surface complexation model, in which the Coulombic term is simply ignored. If charged surface species are included in NEM, their concentrations will be affected by overall chemical equilibrium in the same way as that of the like-charge aqueous ions through the common charge balance and chemical potentials. Hence, SAT will be the only possible type of non-ideality corrections in GEM NEM, whereas in electrostatic SCMs, the Coulombic term is in most cases the strongest non-ideality correction for charged surface species.

3.3. Calculation of surface charge density

Application of any SCM with Coulombic corrections requires that, the surface charge density σ is computed on all surface planes on t-th surface type at each GEM iteration. On the zero plane (the sorbent surface), the net proton charge density is found from mole amounts x of surface complexes:

$$\sigma_0 = \sigma_P + [x(>O_{0.5}H_2^+) - x(>O_{0.5}^-) + x(>O_{0.5}H_2^+L^{l-}) - x(>O_{0.5}^-M^{m+})] /$$

$$/ (X_v M_v A_v \theta_t) \qquad \text{(in mol m}^{-2}\text{)} \qquad (5\text{-}29),$$

where σ_P is the input permanent charge density. In TLM, XTLM and BSM, the charge density formed by outer-sphere surface complexes is calculated separately:

$$\sigma_\beta = [-l \cdot x(>O_{0.5}H_2^+L^{l-}) + m \cdot x(>O_{0.5}^-M^{m+})] / (X_v M_v A_v \theta_t) \qquad (5\text{-}30).$$

Note that in the XTLM for surface ion exchange,

$$\sigma_{X,0} = \sigma_P + [-l \cdot x(>L^{l-}) + m \cdot x(>M^{m+})] / (X_v M_v A_v \theta_t) \quad \text{(inner-sphere)} \qquad (5\text{-}31),$$

$$\sigma_{X,\beta} = [-l \cdot x(>^+L^{l-}) + m \cdot x(>^-M^{m+})] / (X_v M_v A_v \theta_t) \quad \text{(outer-sphere)} \qquad (5\text{-}32)$$

because no amphoteric surface groups and related surface complexes are considered. To calculate surface plane potentials, charge densities should be converted from $\text{mol}\cdot\text{m}^{-2}$ to $\text{C}\cdot\text{m}^{-2}$ units multiplying by the Faraday's constant $F = 96485\ \text{C}\cdot\text{mol}^{-1}$. Another conversion - to express the charge density in nm^{-2} units – requires a multiplication by $6.02214\cdot10^5$.

Note that in GEM-Selektor code, the charge densities used in SCM calculations below, are limited to $|\sigma_o| \le 0.7\ \text{C}\cdot\text{m}^{-2}$ and $|\sigma_\beta| \le 1.7\ \text{C}\cdot\text{m}^{-2}$, otherwise the convergence of GEM algorithm may be destroyed at some first iterations in some systems.

3.4. Triple Layer Model (TLM)

TLM implementation in GEM-Selektor code follows Hayes and Leckie [1987]. In this EDL model (cf. also Fig.3 in [Lützenkirchen, 2002]), the pristine $>O_{0.5}H_2^+$ and $>O_{0.5}^-$ species and inner-sphere surface complexes are assumed to sit on zero plane (sorbent surface) and electrolyte ions approaching the beta plane screen some (de)protonated $> O_{0.5}H^o$ groups, so surface charge densities are calculated from eqns (5-29) and (5-30), respectively. A third, outermost d-plane is located at the distance of closest approach of diffuse layer counter-ions that actually belong to the aqueous phase. Charge density on the d-plane is calculated from the surface charge balance condition:

$$\sigma_0 + \sigma_\beta + \sigma_d = 0 \qquad (5\text{-}33).$$

Note that in GEM approach, a single charge balance constraint is used for the whole system, so in the case of an electrostatic model with a diffuse layer, the sum of total charge amounts on the d-plane of all surface types on all sorption phases will be equal to minus total charge in the aqueous phase, i.e. the latter is no more electroneutral:

$$q_{\text{aq,tot}} = -\sum_\alpha \sum_t \sigma_{d,\alpha,t} X_{\alpha,v} M_{\alpha,v} A_{\alpha,v} \theta_{\alpha,t}\,.$$

However, this has no effect on the stability of aqueous ions because the potential of bulk aqueous phase is always $\Psi_w = 0$ by convention.

The charge-potential relationship in the diffuse layer is described using the Gouy-Chapman equation

$$\sigma_d = -2A\sqrt{I}\sinh\left(F\Psi_d / 2RT\right) \qquad (5\text{-}44),$$

where $A = \sqrt{2 \cdot 10^3 \varepsilon_0 \varepsilon_d \rho_d RT}$, I is the effective molal ionic strength (see eqn 4-3 in **`Activity-Coeffs.pdf`** document), Ψ_d is the relative diffuse-plane potential (V), $\varepsilon_0 = 8.854 \cdot 10^{-12}$ $C^2 \cdot J^{-1} \cdot m^{-1}$ is the dielectric permittivity of vacuum, ε_d is the dielectric constant of the medium in diffuse layer (taken equal to that of water-solvent), and ρ_d is the density of medium (taken equal to that of the bulk aqueous phase, see [Machesky et al., 1998]) at T,P of interest. At ambient conditions, $2A \approx 0.1174$. At low charge density and potential, eqn (5-44) simplifies to $\sigma_d \approx 2.5\sqrt{I} \cdot \Psi_d$ [Dzombak and Morel, 1990].

The value of Ψ_d is obtained from eqn (5-44) solved in the following form [Damaskin and Petriy, 1987]:

$$\Psi_d = \frac{2RT}{F}\operatorname{arcsinh}\left(-\frac{\sigma_d}{2A\sqrt{I}}\right) = \frac{2RT}{F}\ln\left[\sqrt{1+\frac{\sigma_d^2}{4A^2 I}} - \frac{\sigma_d}{2A\sqrt{I}}\right] \qquad (5\text{-}45).$$

Note that in the GEM-Selektor code, thus calculated values of the d-plane potential are limited to $-0.4 \le \Psi_d \le +0.4$ V to ensure a good convergence of the GEM algorithm.

In TLM, the layer between the d-plane (outer Helmholtz plane) and the β-plane (inner Helmholtz plane) is considered as a parallel plane capacitor. The linear change of electric potential between planes is described as

$$\sigma_d = C_2\left(\Psi_d - \Psi_\beta\right) \qquad (5\text{-}46),$$

where C_2 is the input outer capacitance density parameter ($F \cdot m^{-2}$). The relative potential Ψ_β on the β-plane can now be found from eqn (5-46) and used in the Coulombic correction factor $\frac{F}{RT} z_j \Psi_{\alpha,t,\beta}$ for the (electro)chemical potential and activity of any outer-sphere surface complex in eqn (5-5) or (5-4).

Further on, the potential change in the Stern layer between the beta plane and the sorbent surface is considered in TLM as another parallel plane capacitor, where

$$\sigma_0 = C_1\left(\Psi_0 - \Psi_\beta\right) \qquad (5\text{-}47).$$

From this equation, containing an input Stern layer inner capacitance density parameter C_1 ($F \cdot m^{-2}$) and known charge density on zero plane σ_0 (eqn 5-29), the relative potential on zero plane Ψ_0 is calculated. This potential is applied in the Coulombic correction term $\frac{F}{RT} z_j \Psi_{\alpha,t,0}$ for activity and concentration of inner-sphere surface complexes.

A small modification of the GEM TLM (as well as BSM) relative to the original models consists in a possibility to include the density of permanent charge σ_P (an input parameter) into calculation of the zero plane charge density σ_0, as shown in eqn (5-29). Note also that, unlike LMA TLMs, GEM TLMs always converge well.

3.5. Exchange Triple Layer Model (XTLM)

This is a modification of TLM designed for electrostatic SCM modeling of cation binding to permanent charge siloxane surfaces of clay minerals. It resembles the "modified" TLM of Robertson and Leckie [1997] in that the outer-sphere cationic species do not contribute to the charge density on zero plane σ_0 , and are counted in charge density only on the beta plane σ_β with their formula charges, as shown in eqns (5-31) and (5-32). The rest of charge-potential relationships and Coulombic correction factors are calculated as in TLM using eqns (5-33) to (5-47). The inner-sphere cations (presumably Cs+ and H+) contribute to σ_0 charge density only and thus may compensate to some extent a large contribution of permanent charge density affecting the beta-plane potentials.

Usual NEM treatment of the surface ion exchange on clay particles requires quite strong binding constants (10^7 to 10^{12}) of reactions like (5-25) to (5-28) to ensure the full occupation of permanent charge sites at all reasonable pH and aqueous cation concentrations [Fletcher and Sposito, 1989]. GEM NEM for surface ion exchange, in addition, requires strong non-ideal SAT corrections [Kulik et al., 2000], which makes convergence of the GEM algorithm difficult. All this contradicts the weak, mainly electrostatic binding of cations to siloxane planes, inferred especially for clays with octahedral charge like smectites. The new GEM XTLM resolves this contradiction by letting Coulombic terms work directly on "attracting" cations to the siloxane-water interface at quite moderate outer-sphere binding constants (ca. $10^{1.5}$ for monovalent cations or $10^{2.5}$ for divalent cations, reaction 5-27). Although the model is still under testing (Kulik 2003, in preparation), it seems to reproduce correctly (without the mass balance constraint on permanent charge sites) the charge site occupation on smectite interlayer/basal planes over wide intervals of pH and electrolyte concentrations when the TLM capacitance parameters are set to $C_1 = 0.2$ F·m^{-2} and $C_2 = 0.02$ F·m^{-2}. Further work is needed to understand why it was necessary to use so small capacitance parameters.

3.6. Basic Stern Models (BSM and XBSM)

The basic Stern EDL model has one parameter less than the TLM and thus it becomes increasingly used, especially in 1p*K* SCMs including the MUSIC model of Van Riemsdijk and co-workers [see Lützenkirchen, 2002 for details]. In BSM, the potentials on both inner- (Ψ_1) and outer (Ψ_d) Helmholtz planes are taken equal, which makes the second capacitance parameter C_2 obsolete. In the GEM-Selektor implementation, BSM follows the formulation by Christl and Kretzschmar [1999].

Coulombic corrections in BSM are performed as follows. Charge density on the diffuse plane is calculated from the charge balance condition:

$$\sigma_d = -\sigma_0 - \sigma_1 \qquad (5\text{-}48),$$

where charge densities σ_0 and σ_1 are obtained on each iteration of GEM algorithm using eqns (5-29) and (5-30), respectively. In the BSM version for permanent charge ion exchange (XBSM), σ_0 and σ_1 are found using eqns (5-31) and (5-32).

The charge-potential relationship on the d-plane is described by the Gouy-Chapman equation (5-44) and Ψ_d is calculated from eqn (5-45), as in TLM. This immediately gives the potential on the outer Helmholtz plane as

$$\Psi_1 = \Psi_d \qquad (5\text{-}49)$$

and the Coulombic correction factor $\frac{F}{RT} z_j \Psi_{\alpha,t,1}$ for the (electro)chemical potential and activity of outer-sphere surface complexes on t-th surface type in α-th sorption phase (eqns 5-5 or 5-4). Further, the zero-plane potential is calculated as

$$\Psi_0 = {}^{\sigma_0}\!\!/_{C_1} + \Psi_1 \qquad (5\text{-}50),$$

where C_1 ($F\cdot m^{-2}$) is the input inner capacitance density parameter. This potential is applied in the Coulombic correction term $\frac{F}{RT} z_j \Psi_{\alpha,t,0}$ for inner-sphere surface complexes.

Compared to TLM, the BSM usually produces similar fits to titration data at somewhat larger values of C_1 parameter but quite the same values of surface complexation constants. The XBSM is an experimental version of BSM for permanent charge ion exchange surfaces, constructed similar to XTLM (see above). It appears to be less precise in reproducing the total density of exchange cations at varying pH and electrolyte concentrations (a preliminary conclusion).

3.7. Double Layer Model (DLM)

The DLM was probably the most widely used EDL model in the past, due to an excellent book by Dzombak and Morel [1990], and due to implementations in almost every LMA speciation modeling code (FITEQL, PHREEQC, MINTEQA2 etc.). A main argument in favor of the DLM is its simplicity. Compared to the TLM, the DLM has much less adjustable parameters: it ignores formation of outer-sphere complexes and the background electrolyte adsorption, as well as the potential drops within Stern and Helmholtz layers. As a consequence, all surface complexes are considered as inner-sphere, the whole adsorbed charge is assumed to reside on the sorbent surface, and only zero-plane charge density is calculated in the DLM:

$$\sigma_0 = [x(>O_{0.5}H_2^+) - x(>O_{0.5}^-) - (l-h-1)\, x(>H_hL^{(l-h-1)-}) +$$
$$(m-n-1)\, x(>O_{0.5}(OH)_nM^{(m-n-1)+})] / (X_v\, M_v\, A_v \theta_t) \qquad \text{(in mol m}^{-2}\text{)} \qquad (5\text{-}51).$$

From this equation, it becomes clear that each surface complex contributes to the zero plane charge density with its formula charge. Various stoichiometries of cation (M) and ligand (L) charged and neutral surface complexes can be considered (see also eqns 5-21 and 5-22) with $0 \le h \le l$ and $0 \le n \le m$, as well as mono- and polydentate ones. The surface plane potential is assumed to be equal to the diffuse layer potential

$$\Psi_0 = \Psi_d \qquad (5\text{-}52)$$

with the charge balance condition

$$\sigma_d = -\sigma_0 \qquad (5\text{-}53).$$

Values of $\Psi_0 = \Psi_d$ are calculated by solving the Gouy-Chapman equation (5-44), (5-45). The Coulombic correction term $\frac{F}{RT} z_j \Psi_{\alpha,t,0}$ is then applied to all charged surface complexes.

It is clear that the DLM has no adjustable parameters in the charge-potential relationship like TLM or BSM have. In general, the Coulombic correction in DLM is much weaker than that in TLM and, together with ignored electrolyte adsorption, this would result in much stronger fitted intrinsic surface deprotonation constants (and much smaller ΔpK_A values about 2). To counterbalance these strong constants that over-predict (de)protonation more than 2 units away of pH_{PPZC}, relatively small maximum site density parameters must be used (1.5 to 2.5 nm^{-2} or 2.3 nm^{-2} as recommended by Dzombak and Morel [1990]), with the associated SAT contributions in GEM DLMs.

To describe isotherms for the specific adsorption of metal cations, two- or multi-site DLMs are often necessary; at least in some cases, this could be an artifact due to the lack of outer-sphere complexes in the model formulation. It seems that the fitted surface acidity constants in DLM are always a compromise between the model simplicity (outer-sphere electrolyte surface species and capacitance parameters are ignored), the maximum site density, and the need to obtain relatively good fits at moderate ionic strength. In a strict sense, K_{A1} and K_{A2} in DLM are ionic-strength-dependent, and reported intrinsic constants seem to be fitted at ca. 0.1 M ionic strength. To convert the DLM constants for “weak” sites from [Dzombak and Morel, 1990] to thermodynamic constants used in the GEM DLM, a conversion factor -log(3.84/20) ≈ 0.3 pK units must be applied in eqn (5-11) (0.6 units to ΔpK_A in eqn 5-14). For K^{int} of the “strong site” metal surface complexes, the conversion factor about 2 pK units must be applied.

3.8. Constant Capacitance Model (CCM)

The CCM was among historically the first SCMs (suggested by Schindler and coworkers in 1968-72), and probably the simplest one after the NEM [cf. Lutzenkirchen, 2002]. In the classic form, applicable to the systems at constant and high ionic strength of the bulk electrolyte, all surface complexes are assumed to bind directly at zero plane on the sorbent surface. The EDL is considered as a parallel plane capacitor with zero potential at its boundary to the bulk aqueous electrolyte. Thus, the exponential drop of potential in the diffuse layer is ignored, and the whole charge-potential relationships reduces to

$$\sigma_0 = C \cdot \Psi_0 \qquad (5\text{-}54),$$

where C is the EDL capacitance density input parameter ($F \cdot m^{-2}$). The surface charge density σ_0 is calculated using eqn (5-51) analogous to the DLM and using, in principle, the same kind of surface species stoichiometry and the same Coulombic correction factor for charged surface complexes.

The drawback of classic CCM is that it ignores outer-sphere adsorption of electrolyte cations and anions, so the 2pK_A surface deprotonation constants depend on C and site density parameters and have all to be re-fitted at different electrolyte concentrations. For that reason, the GEM-Selektor implementation offers a somewhat more flexible Extended CCM (ECCM), following Nilsson et al. [1996] (cf. also [Lützenkirchen, 2002]). This CCM can be regarded as TLM without the potential decay in the diffuse layer, i.e. with $\Psi_d = 0$, which makes solving the Gouy-Chapman equation obsolete. However, the ECCM allows inclusion of outer-sphere surface complexes (only anionic in the original model of Nilsson, though we do not see any reason against including there also cationic outer-sphere complexes). As in the TLM or BSM, the surface charge densities on zero and beta planes are calculated using eqns (5-29) and (5-30). The charge balance condition is

$$\sigma_\beta = -\sigma_0 \qquad (5\text{-}55).$$

The potentials Ψ_0 and Ψ_β are obtained as follows:

$$\Psi_\beta = -{}^{\sigma_\beta}\!/_{C_2} \qquad (5\text{-}56),$$

$$\Psi_0 = {}^{\sigma_0}\!/_{C_1} + \Psi_\beta \qquad (5\text{-}57),$$

where C_1 and C_2 are input capacitance density parameters ($F\cdot m^{-2}$). Typically, they are constrained by the "total" capacitance parameter C_{tot} by a relation

$$1/C_{tot} = 1/C_1 + 1/C_2 \qquad (5\text{-}58)$$

and first, the fitting of acidimetric titration data is performed using the classic CCM (to which the ECCM reduces when no outer-sphere complexes are included) to obtain C_{tot} and K_{A1}, K_{A2}. Next, the outer-sphere surface complexes are added and their intrinsic constants are adjusted together with the C_1 and C_2 parameters, within the constant C_{tot} constraint eqn (5-58). The ECCM seems to be flexible enough and applicable at relatively low ionic strength (0.1 or so).

4. Surface Activity Terms (SAT)

In GEM SCMs, the SAT is a non-ideality correction that replaces mass balance constraints to mole amounts of surface sites typically used in LMA SCMs. SAT in the only "activity coefficient" of a surface species for the case when the NEM SCM is applied to a given surface type. If electrostatic SCMs are used then the SAT correction interplays with the Coulombic correction factors for charged surface complexes, yet SAT remains the only non-ideality correction for neutral surface species.

The reference state of a surface complex – "infinitely low surface density at infinite dilution of the aqueous sorbate counterpart" (see above) - occurs simultaneously with the "full monolayer coverage at Γ_o" reference state of the "surface solvent" – the $\equiv OH^o$ functional group or the adsorbed water molecule on the bond-saturated surfaces (e.g., siloxane planes). Upon increasing activity of the aqueous sorbate counterpart, still at low concentrations, both the concentration and the activity of the surface complex first increase proportionally to the aqueous sorbate concentration (*linear adsorption region*), displacing the equivalent amount of $\equiv OH^o$ groups or adsorbed H_2O molecules. When the maximum density $\Gamma_{j,t,max}$ is approached closer, the activities of the sorbate and the surface complex both will continue to increase, while the concentration of surface-bound species becomes limited by the density of available sites - a *maximum possible density* of j-th species on t-th surface type $\Gamma_{j,t,max}$.

This kind of behavior is described by Langmuir (or similar) isotherm. It can be shown [Kulik, 2002a] that the Langmuir isotherm equation contains a "site-saturation correction factor"

$$\Xi_j = \frac{\theta_j}{1-\theta_j} \text{ where } \theta_j = \frac{\Gamma_j}{\Gamma_{j,t,\max}},\ 0 < \theta_j < 1, \text{ and } \Xi_j \ge 1 \qquad (5\text{-}59).$$

Note that the fractional surface coverage θ_j *is not the same* as thermodynamic surface concentration Γ_j / Γ_o (eqn 5-2). The difference between the surface density parameters Γ_o and

$\Gamma_{j,t,max}$ is that the former is part of the definition of standard state of surface species – a conventional constant value, whereas the latter is a mineral-surface-specific parameter, which can be fitted or determined from crystallographic or spectroscopic data. This explains why these two parameters are thermodynamically different (although in some cases they may be numerically equal); why thermodynamic concentration of a surface-bound species must be defined via Γ_o but not $\Gamma_{j,t,max}$; and why the $\Gamma_{j,t,max}$ parameter must go into the (non-thermodynamic) value of the site-saturation correction term, called a *surface activity term* (SAT).

When a sorbate binds to specific sites forming a monodentate *j*-th surface complex and no other sorbates compete for these sites, a *non-competitive SAT function* must be applied:

$$\ln \Xi_j^{(n)} = \begin{cases} 0, x_j \le \tfrac{1}{2}\chi_{j,t,L}; \\ \ln x_j - \ln\left(\chi_{j,t,L} - x_j\right) \end{cases} \qquad \text{(5-60)},$$

where $\chi_{j,t,L} = \phi_{\alpha,t} A_{\alpha,v} X_{\alpha,v} M_{\alpha,v} \Gamma_{j,t,max}$ is an *expected maximum mole quantity* of *j*-th surface complex on *t*-th surface type. The SAT equation (5-60) permits to assign *separate maximum densities to reactive sites of different energy on the same surface type without introduction of mass balance constraints*. Calculated between GEM iterations, Eq. (5-60) can reproduce closely the shape of Langmuir isotherm with linear part at low coverages (Ξ_j is truncated to unity at $\theta_j \le 0.5$), bending asymptotically to $\Gamma_{j,t,max}$ at high coverage.

For polydentate surface complexes, it is not yet so clear which kind of SAT has to be applied. The simplest way for a bi-dentate surface complex is to assume that its maximum density is twice less than the maximum monodentate site density, and use eqn (5-60) with this "bidentate maximum density" $\Gamma^{(2)}_{j,t,\max} = {}^{1}\!/_{2} \cdot \Gamma^{(1)}_{j,t,\max}$. Likewise, for 3-dentate species, $\Gamma^{(3)}_{j,t,\max} = {}^{1}\!/_{3} \cdot \Gamma^{(1)}_{j,t,\max}$ should be used, and so on. Note that, at low enough current density. $\theta_j \le 0.5$ in any case, so the SAT will be 1 for surface complexes of any "dentateness" on approaching the reference state. Hence, the dentateness must be accounted for only in the SAT correction factors in GEM SCMs.

If several sorbates compete for the same surface type sites then their *total* must not exceed the *expected total maximum mole quantity of sites* $X_{\alpha,t,L} = \phi_{\alpha,t} A_{\alpha,v} X_{\alpha,v} M_{\alpha,v} \Gamma_{t,L,max}$ for t-th surface type, defined using a *common maximum site density parameter* $\Gamma_{t,L,max}$. Mole quantity of each competing surface complex is then constrained by

$$x_j < \chi_{t,L} \ \text{ where } \ \chi_{t,L} = X_{\alpha,t,L} - \sum_{k \in l_a^{(r)}} x_k \ , \ j \in l_\alpha \backslash l_{\alpha,n} ;\ k \ne j \qquad \text{(5-61)},$$

where $\chi_{t,L}$ is a number of moles of not-yet-consumed "surface solvent", and $l_{\alpha,n}$ stands for a set of non-reacted neutral $\equiv OH^o$ groups, which need a special form of SAT correction (see below) but may be excluded from the GEM model system because they do not influence modeled proton- or ion adsorption curves. A *competitive SAT function* for monodentate binding follows from eqns (5-60) and (5-61):

$$\ln \Xi_j^{(c)} = \begin{cases} 0, x_j \le \tfrac{1}{2}\chi_{t,L}; \\ \ln x_j - \ln\left(\chi_{t,L} - x_j\right) \end{cases} \qquad \text{(5-62)}.$$

Eqn (5-62) is usually applied to outer-sphere surface complexes at relatively high surface coverage, or to cations bound to permanent-charge surfaces, e.g., on clays, expected to compete for the same sort of surface sites of relatively large maximum total density $\Gamma_{t,L,max}$, typically between 1 and 22 sites·nm^{-2} (1.66 to 36.5 μmol·m^{-2}). At the same time, surface complexes compete with aqueous sorbates, as required by the total elemental mass balance in the chemical system and governed by the respective partial molal apparent Gibbs energy values g^o_T. If bi-, tri-, … dentate surface complexes are involved in competition, their mole quantities x must be multiplied by the respective "dentateness" factors (2, 3, …) in eqn (5-61) and (5-62).

On the other hand, specific inner-sphere binding of metal cations to "strong" sites of rather low density (< 0.3 sites·nm^{-2}) must be taken into account in many systems at low coverages and low dissolved metal concentrations. In this case, the competition may be rather difficult to demonstrate, so the "individual" SAT corrections (eqn 5-60) can be applied to all "strong" surface species that can be assigned to the same surface type. This makes the GEM SCM approach flexible in describing trace ion adsorption heterogeneity in GEM SCMs, though more research and testing is still needed.

SAT for >$O_{0.5}$H groups. The simplest case of such a SAT correction occurs if the t-th mineral surface patch, due to crystallographic constraints, can physically hold the surface functional groups at a certain maximum density $\Gamma_{t.max} \neq \Gamma_o$. Then, assuming the constant activity of bulk water $a_w \approx 1$, eqn (5-3) can be rewritten as:

$$\ln x_{jn} \approx \ln 55.5084 + \ln(\phi_{\alpha,t} A_{\alpha,v} M_{\alpha,v} X_{\alpha,v} \Gamma_{\mathrm{o}}) - \ln \Xi_{jn}; \quad \Xi_{jn} = {}^{\Gamma_{\mathrm{o}}}\!/_{\Gamma_{t,\max}} \qquad (5\text{-}63).$$

The surface activity term Ξ_{jn} now represents a constant contribution to chemical potential or activity of the neutral functional group, due to the constant input $\Gamma_{t.\max}$ parameter. In this sense, it can be compared with eqn (5-11) describing the impact of a change in total site density on activity and hence equilibrium constant of a surface complex.

The variable part of SAT must reflect how the "surface solvent" is displaced upon formation of surface complexes. Let

$$\Omega_{\alpha,t} = \sum_{k \in l^{(\mathrm{r})}_{\alpha,\mathrm{t}}} x_k; \quad k \neq jn \qquad (5\text{-}64)$$

stand for a total number of moles of surface complexes on t-th surface type of α-th phase (for polydentate surface complexes, x_k should be multiplied by "dentateness"), and

$$\chi_{tn,\max} = \phi_{\alpha,t} A_{\alpha,v} M_{\alpha,v} X_{\alpha,v} \Gamma_{t,\max} - \Omega_{\alpha,t} \qquad (5\text{-}65)$$

be an expected number of moles of functional groups that remain non-displaced (non-reacted) on that surface type at a prescribed value of $\Gamma_{t,\max}$. Obviously, at the "infinite dilution" of all sorbates, $\Omega_{\alpha t} \Rightarrow 0$, hence $\ln \Xi_{jn} \Rightarrow {}^{\Gamma_{\mathrm{o}}}\!/_{\Gamma_{\mathrm{t,max}}}$, or $x_{jn} \Rightarrow \chi^{\mathrm{o}}_{tn,\max} = \phi_{\alpha,t} A_{\alpha,v} M_{\alpha,v} X_{\alpha,v} \Gamma_{t,\max}$. As the progress of adsorption creates more and more surface complexes, $\Omega_{\alpha t}$ increases, and (as follows from eqn 5-64), $\ln \Xi_{jn}$ must become more positive to keep x_{jn} close to $\chi_{tn,\max}$. In the extreme case, practically all sites will be occupied by surface complexes, that is, $x_{jn} \Rightarrow 0$, $\chi_{tn,\max} \Rightarrow 0$, and $\Omega_{\alpha,t} \Rightarrow \phi_{\alpha,t} A_{\alpha,v} M_{\alpha,v} X_{\alpha,v} \Gamma_{t,\max}$, thus all non-reacted functional groups will be displaced (for instance, as it is usually assumed in 1pK_A SCMs). Such behavior at both limits can be described using a complete SAT function:

$$\Xi_{jn} = \frac{\Gamma_o}{\Gamma_{t,\max}} \cdot \frac{x_{jn}}{\chi_{tn,\max}} \qquad (5\text{-}66).$$

Eqn (5-66) is calculated on iterations of the GEM IPM algorithm (with some precautions against stiff numerical behavior at high coverage of surface complexes). Note that, in practice, there is neither a need to include the non-reacted functional group in GEM SCM modeling runs nor use eqn (5-66). Although numerical calculations involving eqn (5-66) are of theoretical interest only, they may yet be helpful in interpretation of K^{int} values fitted in LMA speciation codes, e.g. in converting them into G^{o}_{298} values to be used in GEM SCMs.

Reciprocity between the SAT and the site-type fraction $\phi_{\alpha,t}$ parameters should be taken into account when modelling non-linear trace metal adsorption isotherms with highest distribution coefficients at lowest surface coverages. One can imagine two physically different situations of location of the so-called "strong metal binding sites" on the mineral surface. (i) there is a small fraction (patch) of the total surface area populated with "strong" adsorption sites, perhaps active for several metal cations that would compete for these sites. (ii) there are some "strong" metal binding sites scattered randomly at a very low density over the homogeneous mineral surface, selective to a given metal cation only. In the GEM approach, the case (i) would correspond to specifying an additional *t*-th surface type having a small $\phi_{\alpha,t}$ parameter (see eqn 5-2) with moderate binding constants for metal surface complexes and (perhaps) competitive SATs. The case (2) would be reproduced by adding "strong" surface complexes to a single surface type (together e.g. with "weak" surface complexes and (de)protonated OH groups). At the same time, such a "strong" surface complex must have a non-competitive SAT controlled by an independent, very small maximum site density parameter $\Gamma_{j,t,max}$. In this case, one should expect a very non-ideal behavior of "strong" surface species at relatively high total metal loadings, when all "strong" sites should be occupied and either "weak" surface binding or precipitation occurs. The right choice of these alternative representations (i) and (ii) depends on the specific microscopic knowledge about the system in question and the related modeling experience is still to be accumulated.

Numerical difficulties with SAT (especially in cases of strong-site or competitive adsorption, NEM SCMs etc.) are common in GEM SCM applications. They result from a stiff nature of the Langmuirian correction factor $\frac{\theta_j}{1-\theta_j}$ (eqn 5-59) that tends to produce very large positive values when the fractional surface coverage θ closely approaches unity (i.e. all accessible sites get occupied by surface complex(es). Between GEM iterations, some SATs may become too large (and mole quantities of respective species will be too suppressed), or too small (mole quantities overthrown) at the next iteration. This may eventually destroy convergence to the minimum or cause infinite oscillations of the non-linear minimization method. Several checks for this situation are included into the high-precision GEM algorithm implementation, though they did not provide a 100% safe effect in all systems. More work is going on in this direction. Convergence problems is common for all highly non-ideal systems, also in LMA methods.

5. Some concluding remarks

Activity of any chemical species can be defined as

$$RT \ln a_j = \mu_j - g^{o}_{j,T} \qquad (5\text{-}67),$$

where the (electro)chemical potential μ_j depends mainly on the bulk composition of the whole aqueous electrolyte - sorbent system and on the species elemental stoichiometry; in GEM-Selektor, any μ_j value can be computed from the species elemental stoichiometry and the "dual solution" elemental chemical potentials. In other words, thermodynamic activity of a species measures a ratio of its current- to the standard/ reference-state concentration in its phase at equilibrium. Conversely, re-arrangement of eqn (5-4) yields

$$\ln x_j = \ln a_j - \ln \Xi_j - \ln(\exp C_F) + \ln\left(\frac{\phi_{\alpha,t} A_{\alpha,v} X_{\alpha,v}}{55.5087 A^o_{\alpha,v}}\right) \qquad (5\text{-}68),$$

where $C_F = \frac{F}{RT} z\Psi$ is the Coulombic term. The rightmost term in eqn (5-68) can be considered constant if the mole quantity of the sorbent $X_{\alpha,v}$ and its molar mass are fixed. The SAT term ln Ξ_j is the only non-thermodynamic concentration correction term in the case of non-electrostatic site-binding model (NEM), where the Coulombic activity coefficient $\gamma_C = \exp(C_F)$ is ignored (set to unity). Away of zero-charge pH point (pH_{PZC}), in the electrostatic SCMs, the C_F term would affect concentration of any charged surface complex even at low surface coverage, where no SAT contribution is expected. At high coverages, the SAT ln $\Xi_j > 0$ comes into play only when the C_F term is insufficient to suppress j-th charged surface complex below the $0.5 \cdot \Gamma_{t,L,max}$ limit, or when C_F enhances concentrations of a surface complex charged opposite to that of the total surface charge and the potential Ψ. Thus, at a given activity a_j, the mole quantity and concentration of a neutral surface complex are affected by the SAT term only, while that of a charged surface species – by interplay between SAT and Coulombic terms.

Note that both Ξ_j and C_F quantities are, actually, physical, non-thermodynamic correction factors, hence validity of thermodynamic treatment of SCMs presented here should not depend on the choice of (non)electrostatic EDL model. Standard partial molal thermodynamic properties of surface species of known elemental stoichiometry must not depend on that choice too. A huge literature exists about the surface charging behavior and the details of the electrostatic phenomena on oxide surfaces – some yet to be accounted for in SAT and Coulombic terms.

A major weakness of 2pK_A SCMs is that involvement of the $\equiv OH^o$ (or $>O_{0.5}H^o$) species, activity of which is constant as long as liquid H_2O is present in the system, makes the LMA-fitted K^{int} values highly sensitive to the site density parameter ($\Gamma_C = \Gamma_T = \Gamma_{max}$) and chosen value of ΔpK_A. The smaller are these two parameters, the stronger are the SAT increments into LMA expressions for the reactions like (5-9) or (5-10) at higher surface coverages. Conversely, the large ΔpK_A and Γ_C parameters (as usually selected in TLM on the background of rather strong Coulombic correction) favour nearly-unity SAT ratios in a very wide interval of surface coverage. Note, that in GEM SCMs, the $>O_{0.5}H^o$ species does not affect the fits to titration data at all and may be dropped from the model system. Hence, the GEM SCMs work, in fact, similar to the 1pK_A LMA SCMs.

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