[AMERICAN JOURNAL OF SCIENCE, VOL. 302, MARCH, 2002, P. 227–279]

GIBBS ENERGY MINIMIZATION APPROACH TO MODELING SORPTION EQUILIBRIA AT THE MINERAL-WATER INTERFACE: THERMODYNAMIC RELATIONS FOR MULTI-SITE-SURFACE COMPLEXATION

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ABSTRACT. A Gibbs energy minimization (GEM) approach to calculate chemical equilibria involving surface complexation at the mineral-water interfaces is presented, permitting the whole continuum "aqueous speciation - heterogeneous adsorption - surface (co)precipitation - solid solution" to be modeled only in elemental stoichiometry, without additional material balance constraints for the total number of surface sites. The thermodynamic stability of surface-bound species is considered in a way similar to that of the solid-solution endmembers, gases, and aqueous species. This consideration is made possible by introducing: (1) the standard and reference states of surface species involving a single value of reference site density Γ_o; (2) an expression of (electro)chemical potential linking quantities of the surface species with the amount and specific surface area of the sorbent; (3) activity/concentration relationships between aqueous sorbates and surface species, based on the surface activity terms (SAT) as functions of the maximum site densities Γ_{max}; (4) the surface type area fractions $\phi_{\alpha,t}$ for describing faces or patches on heterogeneous surface of multi-site-surface sorption mineral phases; (5) an elemental stoichiometry and standard partial molal properties of the amphoteric neutral surface functional group ≡OH and derived surface complexes at ambient conditions, comparable between all (hydr)oxide mineral surfaces. For the ≡OH group (in 2pK$_A$ surface complexation models), a $O_{0.5}H^o$ stoichiometry is conventionally defined from a reaction $0.5H_2O_{aq} = {>}O_{0.5}H^o$, with $\log K_n = 1.74436$ (at $\Gamma_o = 20\ \mu mol \cdot m^{-2}$) which is independent of temperature, pressure, pH, fO_2, amount and specific surface area of the sorbent, aqueous speciation, and surface speciation. It follows that all the non-reacted $>O_{0.5}H^o$ groups have constant activity in the presence of liquid H_2O and are thus macroscopically indistinguishable. The surface heterogeneity is described via standard thermodynamic properties of the surface complexes (reacted groups), such as "surface hydronium" $>O_{0.5}H_2^+$, "surface hydroxyl" $>O_{0.5}^-$, adsorbed cations or anions, as well as through $\phi_{\alpha,t}$ and the common or individual $\Gamma_{t,max}$ parameters. Theoretical findings, implemented in the GEM-Selektor code, are illustrated by modeling the literature potentiometric titration and adsorption data for silica and rutile in NaCl solutions with the triple-layer (TLM), the generalized double-layer (DLM), and the non-electrostatic (NEM) surface complexation models (SCM). Some examples were also calculated with the FITEQL3.2 code to check for compatibility. It is shown: (1) how approximate conversions between partial molal properties of surface species and intrinsic adsorption constants can be performed for different total site densities $\Gamma_C \neq \Gamma_o$; (2) what are the regions of "geometrically ideal" and "non-ideal" adsorption behavior for the chosen SCM and how they are controlled by the SAT = $f(\Gamma_{max})$ on heterogeneous surfaces; and (3) why different sets of TLM parameters are not thermodynamically equivalent, and how a meaningful "optimal" set can be determined from titration data. Due to the separation of Γ_{max} parameters from Γ_o and, hence, from thermodynamic constants, the thermodynamic SCMs (in GEM implementation) can provide more insight into the relationships between surface types, complexes, bulk mineral sorbent, and aqueous sorbates, therefore permitting a more thorough use of microscopic/spectroscopic data in sorption modeling than has ever been possible.

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GLOSSARY OF SYMBOLS

$\in$	belongs to; for instance, $j \in L$ means j belongs to set L
A	stoichiometry matrix in GEM, $A = \{a_{ji}\}, j \in L, i \in N$
$A_o = (\Gamma_o)^{-1}$	reference specific surface area ($5 \cdot 10^4\ m^2 \cdot mol^{-1}$)
$A_{\alpha,v}$	specific surface area of the sorbent of α-th sorption phase ($m^2 \cdot g^{-1}$)
$A^o_{\alpha,v}$	reference specific surface area of the sorbent ($m^2 \cdot g^{-1}$)
A_T	generic total surface area of the sorbent (m^2)
a_{ji}	number of moles of independent component in 1 mole of a dependent component
a	activity of a species (generic)
a^o	activity at the standard state
a_n, a_{jn}	activity of the non-reacted (free) amphoteric surface functional group
a_{aq}	activity of an aqueous species
a_s, a_{ads}	activity of a generic surface-bound species
a_j	activity of j-th surface complex
b	vector of bulk chemical composition in GEM, $b = \{b_i\}, i \in N$
b_i	total number of moles of i-th independent component in the system
C_j	generic concentration of j-th dependent component (species)
C_s	generic concentration of a surface species; C_L is limiting concentration on surface
c_j	energy term for j-th dependent component in GEM (eqs 6, 15, and 18)
C_1	inner-layer capacitance density parameter in TLM ($F \cdot m^{-2}$)
C_2	outer-layer capacitance density parameter in TLM (set to 0.2 $F \cdot m^{-2}$)
Cp^o_j	standard state constant-pressure heat capacity of j-th species at T_o, P_o ($J \cdot K^{-1} \cdot mol^{-1}$)
$\Delta G_{j,s}$	molar surface free energy contribution for j-th sorbent endmember (eq 6)
ΔG^o	$= -2.3026 \cdot R \cdot T \cdot \log K$ - standard Gibbs energy change in reaction ($J \cdot mol^{-1}$)
ΔpK_A	$= pK_{A2} - pK_{A1}$ (reaction 44)
DC	dependent component (species)
DLM	generalized diffuse double layer (surface complexation) model
EDL	electrical double layer (on oxide surface in aqueous solution)
F	Faraday's constant (96'485 $C \cdot mol^{-1}$)
f_j, f_α	Karpov's stability criteria for j-th species and α-th phase (eqs 6 and 15)
fO_2	fugacity of O_2 gas
Φ	$= \{1, 2, \ldots, n(\Phi)\}$ - set of (indices of) phases in GEM system formulation
Φ_s	set of (indices of) sorption phases
$\phi_{\alpha,t}$	fraction of reactive surface area of α-th sorption phase, assigned to t-th surface type
G^o	generic standard molar Gibbs energy
G^o_j	standard Gibbs energy of formation from elements of j-th species at T_o, P_o ($J \cdot mol^{-1}$)
$g_{j,T,P}$	partial molar Gibbs energy function of j-th species at T, P ($J \cdot mol^{-1}$), $g^o_{j,298} = G^o_j$
$g^o_{j,T}$	standard partial molar Gibbs energy function of j-th species at T ($J \cdot mol^{-1}$)
GEM	Gibbs energy minimization
G(x)	scalar total Gibbs energy function of chemical system (eq 1)
$G(x)_j$, $G(x)_\alpha$	increment of j-th dependent component or α-th phase to G(x), respectively
Γ_o	reference (site) density for definition of standard state for surface species, set to 20 $\mu mol \cdot m^{-2} \approx 12.05\ nm^{-2}$
Γ_C	conditional total (site) density, $\Gamma_C \neq \Gamma_o$ ($\mu mol \cdot m^{-2}$ or nm^{-2})
Γ_T	generic total site density parameter (nm^{-2}), 1 nm^{-2} = 1.66054 $\mu mol \cdot m^{-2}$
Γ_{max}	maximum (site) density, assigned separately to a single j-th surface complex (non-competitive adsorption, $\Gamma_{j,max}$) or to a t-th surface type (competitive adsorption, $\Gamma_{t,max}$)
Γ_j	actual density of j-th surface species ($\mu mol \cdot m^{-2}$)
Γ_{jn}	density of the neutral amphoteric surface functional group ($\mu mol \cdot m^{-2}$)
$\Gamma_{s,max}$	generic maximum density of adsorbed species
γ_j	activity coefficient (in practical concentration scale for aqueous species)

I	effective molal ionic strength in aqueous electrolyte, mol · $(kgH_2O)^{-1}$
IC	independent component (stoichiometry unit) in GEM formulation
H^o_j	standard enthalpy of formation from elements of a j-th species at T_o, P_o (J · mol^{-1})
K	thermodynamic equilibrium constant; K_j - that of formation of j-th species
K_{A1}, K_{A2}	thermodynamic surface deprotonation constants in single-site $2pK_A$ SCMs
$\log K_{A12}$	$= \log K_{A1} + \log K_{A2}$ (reaction 43)
K_{Na}, K_{Cl}	thermodynamic equilibrium constants of outer-sphere adsorption in $2pK_A$ TLM
K_M	thermodynamic equilibrium inner-sphere metal adsorption constant
K^{int}	intrinsic equilibrium surface complexation constant
K_d	distribution constant (also related to Langmuir isotherm)
K_h	Henry thermodynamic constant
K_w	thermodynamic constant of water dissociation reaction, $H_2O = H^+ + OH^-$
K_n	thermodynamic equilibrium constant of a reaction of formation of the amphoteric neutral surface functional group $0.5H_2O_{aq} = {>}O_{0.5}H^0$, $\log K_n = 1.74436$
K_o	intrinsic solubility product of the sorbent end member
K_s	surface-perturbed solubility product of the sorbent endmember
k_α	shape/size factor of the particulate/porous sorbent (sec. 1.2.2)
L	set of (indices of) all dependent components in GEM chemical system formulation
LMA	law of mass action
l_α	set of (indices of) dependent components included into α-th phase
$l_{\alpha,v}$	set of (indices of) sorbent-part end-members of α-th sorption phase
$l_{\alpha,s}$	set of (indices of) surface complexes on α-th sorption phase
$l_{\alpha,n}$	set of (indices of) non-reacted functional groups on α-th sorption phase
m	molality, mol · $(kgH_2O)^{-1}$
m_n	molality of non-reacted neutral amphoteric surface functional group
m^o_n	expected maximum molality of neutral amphoteric surface functional group at Γ_o
m_j	molality of j-th surface complex
$M_{\alpha,v}$	molar mass of the sorbent part of α-th sorption phase (g · mol^{-1})
μ_j	(electro)chemical potential of a j-th dependent component (species), mol · mol^{-1}
μ^o_j	standard-state chemical potential of a j-th dependent component
μ^o	generic standard-state chemical potential
NEM	non-electrostatic (surface complexation) model
N	set of (indices of) independent components forming stoichiometry basis of the chemical system
$N_{t,s}$	LMA SCMs constraint on total number of moles of surface sites
$n(\Theta)$	number of elements in a finite countable set Θ
$>O_{0.5}H^0$	neutral surface functional group, considered in GEM SCMs in $O_{0.5}H$ elemental stoichiometry
$>O_{0.5}H_2^+$	protonated amphoteric surface group in GEM SCMs ($O_{0.5}H_2^+$)
$>O_{0.5}^-$	deprotonated amphoteric surface group in GEM SCMs ($O_{0.5}^-$)
$>O_{0.5}^-Na^+$	outer-sphere surface complex of Na^+_{aq} in GEM TLM ($O_{0.5}Na$)
$>O_{0.5}H_2^+Cl^-$	outer-sphere surface complex of Cl^-_{aq} in GEM TLM ($O_{0.5}H_2Cl$)
$\Omega_{\alpha,t}$	total moles of surface complexes on t-th surface type of α-th sorption phase (eq 34)
$\equiv$	denotes a generic surface-coordinated species
Ψ	generic surface electrostatic potential (V, volts)
$\Psi_{\alpha,t}$	relative electrostatic potential (V) referred to certain EDL plane according to the chosen SCM for t-th surface type on α-th sorption phase.
Ξ_j	surface activity term (SAT) for a j-th monodentately-bound surface complex
Ξ_{jn}, Ξ_n	complementary SAT for the neutral amphoteric surface functional group
P	pressure (bar); P_o - reference pressure (1 bar)
p	vector of Lagrange multipliers related to metastability constraints (eq 4)
$pK = -\log K$;	$pH = -\log \{H^+_{aq}\}$, {} denotes activity (in molal scale) here
pH_{PPZC}	pH point of pristine zero charge

pH_{PZC}	(measured) pH point of zero charge
q	constant multiplier for site density conversions (eq 20)
$\bar{r}_j$, $\underline{r}_j$	upper- and lower metastability constraints to x_j, $(\bar{r}_j, \underline{r}_j) \in \Re$
$\Re$	set of additional metastability constraints in GEM (eq 3)
R	universal gas constant ($8.3144 \, J \cdot K^{-1} \cdot mol^{-1}$)
R_d	empirical distribution ratio coefficient (in sorption experiments, $cm^3 \cdot g^{-1}$)
S_j^o	standard state absolute entropy of a j-th species at T_o, P_o ($J \cdot K^{-1} \cdot mol^{-1}$)
SAT	surface activity term
SCM	surface complexation model
SSAS	solid solution–aqueous solution (system)
$\sigma_{j,v}$	specific surface free energy in water for pure sorbent endmember ($J \cdot m^{-2}$)
σ_H	total proton surface charge density ($\mu mol \cdot m^{-2}$)
T	temperature, K (°C, if indicated); T_o - reference temperature, 298.15 K (25°C)
TLM	triple layer (surface complexation) model
$\Theta_{\alpha,v}$	asymmetry term for the sorbent end-members (eqs 6 and 17), uses $\theta_o = A_{\alpha,v} M_{\alpha,v} \Gamma_o$
$\Theta_{\alpha,s}$	asymmetry term for the surface species on α-th sorption phase (eqs 15 and 16)
θ	fractional surface coverage on a surface type (relative to $\Gamma_{t,max}$)
u	GEM dual solution vector $u = \{u_i\}$, $i \in N$
u_i	equilibrium chemical potential of i-th independent component ($mol \cdot mol^{-1}$)
υ_j	approximation of (electro)chemical potential μ_j at iterations of GEM algorithm
V_j^o	standard-state volume of a j-th species at T_o, P_o ($cm^3 \cdot mol^{-1}$)
x	GEM prime solution vector $x = \{x_j\}$, $j \in L$
x_j	number of moles of j-th dependent component (species); $\hat{x}_j$ - at equilibrium
x_w, x_{jw}	number of moles of water-solvent in aqueous electrolyte
x_n, x_{jn}	number of moles of (non-reacted) neutral amphoteric surface functional groups
X_α	total number of moles of dependent components in α-th phase
$X_{\alpha,v}$	total number of moles in the sorbent (volume) part of α-th sorption phase
$X_{\alpha,t,L}$	expected total number of moles of competing surface species (eq 30)
X-	ion-exchange binding site on a permanent-charge mineral surface
χ_n	expected number of moles of surface functional groups at reference density Γ_o
$\chi_{j,t,L}$	expected limiting number of moles at maximum density of j-th surface species
$\chi_{t,L}$	maximum expected number of moles of a competing species (eq 31)
$\chi_{tn,max}$	expected number of moles of non-reacted surface functional groups (eq 35)
$\chi_{\alpha,t}^o$	maximum expected number of moles of monodentate species on t-th surface type
z_j	effective charge of j-th species, equals formula charge for all aqueous and surface species, except $>O_{0.5}^{-}Na^{+}$ (z = 1) and $>O_{0.5}H_2^{+}Cl^{-}$ (z = −1)

INTRODUCTION

Recent efforts in geochemistry, soil science, and aquatic chemistry have been dedicated to studies of reactivity and sorption at the mineral-water interfaces (Sposito, 1984; Brümmer and others, 1988; Davis and Kent, 1990; Dzombak and Morel, 1990; Goldberg, 1992; Stumm, 1992; Barrow and others, 1993; Morel and Hering, 1993; Charlet, 1994; Langmuir, 1997; Zachara and Westall, 1999, and references therein) because such phenomena govern the retention of trace elements and organic substances of environmental concern and the kinetics of mineral dissolution/precipitation. The more experimental data are accumulated, the more robust theoretical models of sorption on heterogeneous mineral surfaces are required. However, a unified thermodynamic model, capable of accounting for the most important physicochemical interactions at the mineral-water interface, still needs to be developed and implemented in geochemical modeling computer codes.

Two theoretical approaches have been commonly used so far: (1) (semi)empirical equations of *adsorption isotherms* (Langmuir, Freundlich, Frumkin); (2) mechanistic *surface complexation models* (SCM). A particular set of isotherm parameters is applicable only to the range of conditions where the empirical data have been obtained. This limitation probably provided a major impetus for the advancement of SCMs, which can be defined as *chemical models based on molecular descriptions of the electrical double layer with equilibrium-derived adsorption data* (Goldberg, 1992). Adjustable parameters of SCM are fitted against experimental titration data graphically or using programs such as FITEQL (Herbelin and Westall, ms, 1996). Thus, the obtained parameter sets can often describe sorption data over broad ranges of varying pH, ionic strength, dissolved metal and particle concentrations. The use of advanced SCMs such as the Triple Layer Model (TLM) for fitting metal adsorption data obtained at different ionic strengths (*I*) may suggest the "outer-sphere" (dependent on *I*) or the "inner-sphere" (independent of *I*) surface complexation mechanism (Hayes and Leckie, 1987; Hayes and others, 1988; Davis and Kent, 1990). There was an alternative opinion that different SCMs and parameter sets can fit the same titration data equally well (Westall and Hohl, 1980), that is, the SCM fits cannot provide insights into the actual sorption mechanisms.

This controversy has been a driving force for the further development of thermodynamic sorption models. So far, only a few studies have added surface precipitation to SCM (Farley and others, 1985; Katz and Hayes, 1995; Lützenkirchen and Behra, 1996; Karthikeyan and others, 1997). An ultimate need in modeling sorption is to add surface precipitation and solid solution formation to the integral model description of processes at mineral-water interfaces (Scheidegger and Sparks, 1996; Kersten and Böttcher, 1997). Various microscopic phenomena must be translated into thermodynamic properties and constraints for surface types, sites, species, phases, and the whole chemical system. Some of such properties become predictable in a consistent crystallochemistry-based approach to the assessment of site types and densities on oxide and silicate minerals (Koretsky and others, 1998), pH of zero charge (Sverjensky and Sahai, 1996), intrinsic TLM adsorption constants (Sahai and Sverjensky, 1997a,b) and capacitance density parameters (Sverjensky, 2001).

The success of Sverjensky's approach can be understood by assuming that stoichiometry and thermodynamic properties of surface species are much more influenced by the solid sorbent structure than by the surrounding bulk aqueous electrolyte. Further developments in thermodynamic sorption modeling need to consider the "sorption phase" (combining a solid mineral sorbent with the surface species coordinated on different particle faces) as being more similar to a (non-ideal) solid solution phase than to the aqueous electrolyte. However, it is hardly possible to use any of the available "volume" solid solution models describing non-ideal or ideal mixing on single- or multiple crystal lattice sites (see, for instance, Anderson and Crerar, 1993) directly for surface complexation. The "volume" solution models lack some relevant features, namely, the explicit surface area and site density parameters; the surface charge – potential relationships necessary to account for EDL interactions; and the essentially "dimeric" nature of adsorption, assumed to occur within a monolayer of physically adsorbed water molecules.

Traditionally, SCMs have been implemented in several computer codes (such as MINEQL, FITEQL, Geochem, MINTEQA, GWB, PHREEQC) based on the so-called Law-of-Mass Action (LMA) algorithm (Smith and Missen, 1982; Morel and Hering, 1993; Bethke, 1996; Zachara and Westall, 1999; Parkhurst and Appelo, 1999). Surface species are treated in the LMA technique much in the same way as aqueous species, but subject to additional material balance constraints for the total number of moles of surface sites $N_{t,s}$ (plus Coulombic term corrections and EDL surface charge balance for the electrostatic SCMs). Links to composition, quantity, specific surface area, and site density parameters of the solid sorbent are thus embedded only in the $N_{t,s}$ values but not explicitly considered in the mathematical structure of the LMA equilibrium speciation problem. In other words, the "palette" of LMA technique (in the case of

NEM, only log K^{int} values and $N_{t,s}$ constraints) is not rich enough for expressing detailed knowledge about mineral surface sites and types at the molecular scale. Composition and stability of the sorbent, totally hidden in the $N_{t.s}$ values, are not considered at all in the LMA algorithm. In the case of multiple $N_{t,s}$ constraints, information about how many sorption phases are present in the system, which sorbents are stable or metastable, and how the site types are distributed between the sorbents and surfaces is, in principle, kept only in the modeller's mind. Perhaps, this important limitation has slowed down the progress in utilizing spectroscopic and microscopic data on surface species, surface/site heterogeneity and structure of mineral-water interface in thermodynamic sorption modeling.

To overcome the above limitations, the author attempted to apply an alternative Gibbs energy minimization (GEM) approach to calculate sorption equilibria (Kulik, 1995, 1998, 2000; Aja and Kulik, ms, 1997). The GEM SCM technique extends the *convex programming* approach of Karpov, Chudnenko, and Kulik (1997) and considers the thermodynamic stability of surface species in a way similar to that for the solid-solution endmembers, gases, and aqueous species, subject only to elemental (and charge) material balance constraints for the whole chemical system; no additional $N_{t,s}$ constraints for surface site types are necessary. However, the implementation of GEM SCM technique has led to the re-investigation of some key theoretical issues such as: (1) standard and reference states for surface species; (2) activity/concentration relationships between aqueous, surface, and sorbent species; (3) account for surface heterogeneity in the structure of thermodynamic models of multi-site-surface sorption phases; (4) stoichiometry and standard partial molal properties of the neutral amphoteric ≡OH functional groups and derived surface complexes; and (5) conversions between intrinsic and thermodynamic adsorption constants and partial molal properties of surface species. Consistent answers to these questions would undoubtedly be helpful in developing a unified thermodynamic description of sorption - solid solution - aqueous solution interactions, thus closer approaching the complexity of the mineral-water interface.

The GEM SCM technique was first implemented in Selektor-A code and successfully applied in the interpretation of the potentiometric titration and REE adsorption data on Marblehead illite (Aja and Kulik, ms, 1997; Kulik and others, 2000a); potentiometric data for rutile to 250°C (Kulik, 2000), as well as adsorption and ion exchange on marine MnO_x (Kulik and Kersten, 1998; Kersten and Kulik, in preparation). The most recent, user-friendly cross-platform GEM-Selektor code and database increase the applicability of the GEM technique to sorption modeling (version 2-PSI for Win32 and Linux, http://les.web.psi.ch/Software/GEMS-PSI/).

Note that the theoretical basis, numerical algorithms, input, and output data appear rather different, if LMA and GEM techniques and software are compared. The former technique (LMA) is considered in textbooks (Morel and Hering, 1993; Bethke, 1996) and included in widespread computer codes, such as FITEQL (Herbelin and Westall, ms, 1996), Geochemists Workbench^{TM} (Bethke, 1996) and PHREEQC2 (Parkhurst and Appelo, 1999), which became, in fact, the standard tools in processing aqueous speciation, adsorption, and ion exchange data. The latter technique (GEM) is not yet as readily available and is far less well known. Thus, its further promotion needs a more detailed description and clear demonstration of its capabilities, beginning with the well-known systems and experimental data already considered using the LMA codes.

Therefore, the *first goal* of this contribution was to describe the thermodynamics of surface complexation and the algorithms used for adding them to the GEM convex programming framework and algorithms. Here, theoretical issues will be addressed and illustrated by examples of model potentiometric titrations of oxides using the triple-layer (TLM), double-layer (DLM), and non-electrostatic (NEM) models. Some examples were also computed using the FITEQL3 LMA code; a detailed comparison of GEM and LMA sorption modeling is to be provided elsewhere (Kulik and Peretyashko, 1998; *ms* in preparation).

The *second goal* is to establish internally consistent values for thermodynamic adsorption constants and standard partial molal thermodynamic properties of the amphoteric neutral surface ≡OH functional group and other surface species considered in $2pK_A$ SCMs under ambient conditions. The achievement of this goal would open the way for the development of a unified thermodynamic database for surface species, applicable for different surfaces and sorbents, and consistent with the data for minerals, gases, and aqueous species, available, for instance, in the SUPCRT92-98 database (Shock and others, 1997). A straightforward extension to hydrothermal conditions has been demonstrated elsewhere (Kulik, 2000).

PART 1. MODELING TECHNIQUES

1.1. The LMA Framework and Algorithms

The LMA algorithms (for details, see Bethke, 1996; Parkhurst and Appelo, 1999; Zachara and Westall, 1999) differentiate between the *total balance constraints* N_t on the *constituents* comprising the system composition (usually number of moles of aqueous ions and surface sites per 1 kg H_2O); the *master species* (aqueous ions and surface sites with unit stoichiometry made up of only one constituent), the concentrations of which are taken directly into the material balance equations; and the *product species* (aqueous complexes, surface complexes, gases, and minerals) linked to the master species via the LMA expressions and equilibrium constants K of the respective complexation or dissolution reactions. The system of constituent material balance equations is then iteratively solved together with the system of LMA equations for obtaining the full equilibrium speciation (that is, concentrations of all master and product species) using the Newton-Raphson or a similar numerical algorithm. To convert between activities and concentrations of aqueous species, the activity coefficients (and Coulombic terms for charged surface species) are computed at iterations from the Davies, Debye-Hueckel, Gouy-Chapman, or other appropriate equations. Subdivision of the chemical system into thermodynamic phases (with concentrations of species scaled to the amount of its host phase) is usually not performed in the LMA codes, at least not in those where surface speciation is implemented. In other words, only one (aqueous) multi-component phase of variable composition is considered mathematically. Other phases, for example, minerals, can be taken into the LMA tableau as fixed-composition species only, described by their stability constants.

Modeling of the solid solution-aqueous solution (SSAS) systems is difficult in the LMA approach because knowledge of mole fractions of the solid solution endmembers (and weighted total solubility product of the solid solution) at equilibrium with aqueous electrolyte is required. The aqueous speciation, in turn, depends on the quantity and composition of solid solution phase, and both are, in principle, unknown at the beginning of speciation calculations. For the binary (non-ideal) SSAS systems, the problem can be circumvented by application of Lippmann diagrams (Glynn and Reardon, 1990) and respective software enhancements (MBSSAS code, Glynn 1991; PHREEQC2 code, Parkhurst and Appelo, 1999). Even Lippmann diagrams, however, become intractable for higher-order SSAS systems, which can only be directly solved using GEM algorithms (Kulik and others, 2000b). Hence, there is no efficient way to consider many surface species together with sorbent endmember(s) similarly to SSAS equilibria using the LMA approach, especially if several sorption phases are involved.

Perhaps for the above reasons, surface complexes are traditionally treated in the LMA approach in the same way as aqueous complexes (formally speaking – as part of the aqueous phase), but subject to additional balance constraints for the total number of surface sites $N_{t,s}$ and surface charge $N_{t,e}$. As mentioned in the Introduction, all information about the sorbent, its quantity, stability, structure, composition, specific surface area, distribution of site types on surface, et cetera, is hidden within the $N_{t,s}$ constraints but not included in the explicit mathematical structure of the LMA equilibrium speciation problem. The $N_{t,s}$ balance constraints are so strong that any calculated aqueous - surface speciation is "apparently successful". However, such calculations reflect our a priori guesses to a much greater extent than they elucidate the relative (meta)stabilities of aqueous, gaseous, solid-solution, and sorption multicomponent phases potentially appearing at the equilibrium state at a given bulk composition of the whole system, and how these relative stabilities would affect speciation in each of these phases. The last statement needs more explanation (provided below in sec. 1.2.3).

However, the LMA algorithms do have numerous advantages, for instance: (1) simple theory and mathematical definitions, often claimed to be equivalent to that of the GEM approach (for instance, by Smith and Missen, 1982); (2) quite good mass balance precision and fast convergence of the numerical algorithms; (3) simple, compact, and transparent program codes (MINEQL, PHREEQC); (4) no need in thermochemical data for the master species; (5) the thermodynamic data needed are $\log K = f(T)$ for the product species only. Nevertheless, a clarification of the choice of standard and reference states and an understanding of the factors influencing values of intrinsic adsorption constants would only enhance the performance and reliability of LMA SCM approach.

1.2. The Gibbs Energy Minimization (GEM) Approach

The GEM convex programming approach (Karpov and others, 1997; 2001) is based on an explicit consideration of independent components, dependent components, and phases.

Independent components (IC) are stoichiometric units in which the bulk composition of chemical systems (and formulae of all relevant chemical species) can be expressed in the most general and unconstrained way. Natural choices for IC are chemical elements and charge.

Dependent Components (DC, or species) are any compounds of a definite stoichiometry constructed from a given set of independent components. If chemical elements are taken as IC, then the stability of each j-th DC (at reference temperature and pressure) is defined by its molar Gibbs energy of formation G_j^o from IC in their respective standard states. G_j^o values (and other standard thermodynamic properties) are available from chemical thermodynamic databases such as SPRONS92-98 (Shock and others, 1997, and references therein). Dependent components are taken into the overall material balance (set by total number of moles of independent components) using their elemental stoichiometries (formulae), each expanded into one row of the stoichiometry matrix A (see below).

Phase definitions (or simply *phases*) each include one or several dependent components and describe thermodynamic phases that may (or not) appear in the final equilibrium state. An important difference between LMA and GEM algorithms is that the GEM treats activities and concentrations of DCs separately in each phase, taking into account the appropriate standard concentration scales. Conversely, it is possible in the GEM approach to solve equilibria directly, even in complex systems containing several (non)ideal solid solutions, gas mixture, aqueous electrolyte, and more single-component condensed phases than is allowed by Gibbs phase rule.

The GEM algorithm splits the input bulk elemental composition of the system into quantities of all species and stable phases such that the total Gibbs energy G(x) is minimized, subject to the material balance constraints on IC, kinetic restrictions on

TABLE 1

Input and output data in GEM IPM algorithm (see also Glossary of Symbols)

Input Data	**Output Data**
N - set of independent components (IC)	
L – set of dependent components (DC)	x – moles of DC at equilibrium (prime solution)
Φ - set of phases, $n(\Phi)$ may exceed $n(N)$	f_α - Karpov stability criteria for phases
A – formula stoichiometry matrix for DC	
b – bulk chemical composition, moles of IC	u – vector of chemical potentials of IC at equilibrium state (dual solution)
T – temperature; P – pressure of interest	
$g_{T,P}$ – vector of partial molar Gibbs energy functions at T,P for DC	υ - chemical potentials of DC at equilibrium state
Parameters and equations for calculation of activity coefficients; metastability constraints	γ - vector of DC activity coefficients (SAT values for sorbates)
Optional: specific surface area and surface free energy of solid sorbents; parameters of surface (site) types	Secondary: concentrations of species in phases, equilibrium pH, pe (Eh) values, partial pressures of gases; surface densities of adsorbed species, distribution coefficients, et cetera

some DC, and thermodynamic properties of phases and their components. The input and output data sets required by the GEM technique are listed in table 1. In a formal algebraic notation, l_α stands for a set of indices of DC included into α-th phase, $n(l_\alpha) \geq 1$; X_α denotes quantity of this phase:

$$X_\alpha = \sum_j x_j, \qquad j \in l_\alpha$$

where x_j stands for number of moles of j-th species. Let υ_j be an approximation of the chemical potential of j-th species, expressed via the standard chemical potential function $g_{j,T,P}/(RT)$ (R is universal gas constant, T is temperature, K), concentration, and activity coefficient in the respective phase. G(x) is then a scalar total Gibbs energy function of the system:

$$G(x) = \sum_j x_j \upsilon_j, \qquad j \in L \tag{1}$$

Equilibrium speciation in the chemical system – the sought-for vector $x = \{x_j\}$, $j \in L$, moles of all n(L) dependent components in all phases – can be found by minimizing total Gibbs energy:

$$G(x) \Rightarrow \min \qquad \text{subject to } Ax = b,\ x \in \Re \tag{2}$$

where $A = \{a_{ji}\}$, $j \in L$, $i \in N$ is a stoichiometry matrix (a_{ji} is number of moles of i-th IC in one mole of j-th DC); $b = \{b_i\}$, $i \in N$ is an input vector of the total bulk chemical composition of the system (b_i is total number of moles of i-th IC in the system); and $\Re$ stands for a set of lower-, upper- or two-side metastability constraints to the sought-for x_j values:

$$\text{trivial: } x_j \geq 0; \qquad \text{non-trivial: } \underline{r}_j \leq x_j \leq \bar{r}_j,\ j \in \Re \tag{3}$$

It follows from the theory of mathematical programming that a vector $\hat{x}$ will be an optimal *prime solution* of the problem (eq 2) if and only if such vectors of the Lagrange multipliers $u = \{u_i\}$, $i \in N$, and $p = \{p_j\}$, $j \in \Re$ exist that the *Kuhn-Tucker duality conditions of optimality* are satisfied (Karpov and others, 1997; 2001):

$$\begin{gathered} \upsilon - A^T u + p \geq 0, \\ (\upsilon - A^T u + p)(\underline{r} - \hat{x})^T = 0, \\ p \geq 0,\ p(\hat{x} - \bar{r})^T = 0, \\ A\hat{x} = b \end{gathered} \tag{4}$$

In equations (4), the elements of the optimal *dual solution* vector u are chemical potentials of independent components at the equilibrium state; the non-zero p_j multipliers apply to the metastable (restricted by eq 3) species only; and ^{T} is the transpose operation. In fact, application of the Kuhn-Tucker conditions (4) makes the GEM approach mathematically not equivalent to the LMA approach in a sense that the LMA yields the prime solution vector x only, while the GEM also can provide the dual solution vector u connected to the x vector via the υ vector and the A matrix. Equations (4) are utilized in an iterative solution of the problem (eq 2) using the *Interior Points Method (IPM)* non-linear minimization algorithm (Karpov and others, 1997). Application of the IPM to calculation of chemical equilibria requires knowledge of consistent expressions for:

(1) increment of j-th species to the total Gibbs energy, $G(x)_j$;
(2) prime chemical potential function of j-th species υ_j;
(3) Karpov's stability criteria for j-th species f_j and α-th phase f_α;
(4) equations for the activity coefficients γ_j of species in the non-ideal multicomponent phases.

Such a set of expressions, reduced into the uniform rational concentration scale, has been first derived for the aqueous electrolyte, gas (plasma), single-, and multicomponent condensed phases by Karpov (1981; see also eqs 2, 6, 7, and 8 in Karpov and others, 1997). In the present contribution, the consistent $G(x)_j$, υ_j, f_j and γ_j expressions will be provided for a sorption phase combining the solid sorbent with associated surface species. Using such expressions, it becomes possible to calculate the surface complexation equilibria involving several sorbents in mathematically the same way as the "usual" multiphase SSAS systems, that is, with material balance constraints set only for the total number of moles of independent components (chemical elements and charge).

1.2.1. Conceptual framework.—A *sorption phase* entity forms the basis of the unified treatment of solid-solution - sorption - aqueous-solution equilibria in the GEM approach. The sorption phase definition consists of two parts. A *sorbent part* of the α-th

TABLE 2

Standard and reference states of the non-surface species

#	**Phase and species type**	**Standard state** $\mu^o = g^o/(RT)$	**Reference state**
1	Solid and liquid condensed phase species	1 mole at T	Pure substance
2	Gases	1 mole at P_o = 1 bar, T	Pure ideal gas at P_o
3	H_2O - solvent of aqueous electrolyte	1 mole at T	Pure H_2O – solvent
4	Aqueous species (ions, complexes, dissolved gases)	1 mole per 1 kg H_2O at T (1 molal)	unimolal at hypothetical "infinite dilution"

phase (indexed with v - volume) includes one or more condensed endmembers; it is assigned with certain specific surface area $A_{\alpha,v}$ ($m^2 \cdot g^{-1}$) and specific surface free energy of endmember in pure water $\sigma_{\alpha,v}$ ($J \cdot m^{-2}$), both values assumed constant. A *surface part* consists of a monolayer of non-reacted amphoteric neutral ≡OH functional groups coordinated to the sorbent surface at the total site density Γ_C. Part of these groups can react and/or be replaced by one or more *surface complexes* (indexed with j) up to their own maximum densities Γ_{max} (equal or not equal to each other and to Γ_C) on one or more *surface types* on the sorbent (indexed with t; for example, different faces of crystalline particles). Each surface type occupies a prescribed *effective fraction* $\phi_{\alpha,t}$ of the sorbent total surface area $X_{\alpha,v}\, M_{\alpha,v}\, A_{\alpha,v}$, where $M_{\alpha,v}$ is a sorbent mass per mole ($g \cdot mol^{-1}$), and $X_{\alpha,v}$ stands for the actual number of moles of the sorbent,

$$X_{\alpha,v} = \sum_j x_j, \qquad j \in l_{\alpha,v} \tag{5}$$

The constant product $\phi_{\alpha,t} \cdot A_{\alpha,v}$ can be considered as an additional thermodynamic factor of state defining the behavior of t-th surface type. This factor permits the activity and concentration of a surface species on t-th surface type to be linked to the quantity $X_{\alpha,v}$ of the sorbent *without an extra material balance constraint,* if the standard and reference states of the surface species are unequivocally defined in such a way that they are consistent with those for the condensed phases, gases and aqueous species.

As there are excellent textbooks discussing the standard and reference states (for instance, Anderson and Crerar, 1993; Nordstrom and Muñoz, 1994), only the conventions used by Karpov and others (1997) are summarized in table 2. The standard state implies that no external fields (electrical, electromagnetic, et cetera) are operating, and the standard chemical potential of a substance, $\mu^o \cdot RT$, equals its molar Gibbs energy of formation from chemical elements at standard states, G^o. The standard state of an element is its most stable phase state at the reference temperature T_o = 25°C and pressure P_o = 1 bar. Absolute values of G^o and μ^o cannot be known; at ambient conditions (P_o, T_o), the G^o values are conventionally set to zeros for all elements and electrical charge. Electrochemical conventions set all partial molal properties of the aqueous H^+ ion to zeros at all T,P ("standard hydrogen scale"); the same applies to g^o_T values of the fictive "aqueous electron" (e-) species.

TABLE 3

Transformations from standard states to states of interest for the non-surface species

#	Step	Description
1	From P_o, T_o to P, T of interest	Calculation of the partial molal (molar) Gibbs energy function $g_{j,T,P}$; addition of ln P for gases
2	From standard-state a_o to arbitrary activity a_j	Addition of ln a_j term to $\mu^o_j = g_{j,T,P}/(RT)$
3	From reference state (ideal) to non-ideal state	Splitting the ln a_j term to ln C_j + ln γ_j where ln $\gamma_j \neq 0$ (or ln m_j + ln γ_j where ln $\gamma_j \neq 0$ for aqueous species); γ_j are non-thermodynamic functions of composition, temperature and pressure
4	From practical to rational scale of concentrations	Molality – to mole-fraction conversion (addition of $\ln(1000/M_{H2O}) - \ln C_{H2O}$, non-logarithmic terms)
5	From zero surface energy (if $\sigma_{j,v}$ is known)	Addition of $\Delta G_{j,s} = \frac{2}{3} k_\alpha A_{\alpha,v} M_{\alpha,v} \sigma_{j,v}$ term to $g_{j,T,P}$ for the sorbent endmembers (optional)

The reference state of a j-th species in α-th phase is understood here as a (unit) concentration C_j being equal to activity $a_j = C_j \cdot \gamma_j = \mu_j - \mu_j^o$ - const, implying that the activity coefficient $\gamma_j = 1$ in absence of any non-ideal interactions with other species in this phase. For condensed phases, water-solvent in aqueous electrolyte, and gases, the rational (mole-fraction) scale of concentrations is used. For the aqueous species, the practical (molal) scale of concentrations m_j, activities $m_j\ \gamma_j$ and activity coefficients γ_j (expressed in moles per 1 kg of H_2O solvent) is more convenient and usual in thermodynamic calculations (Anderson and Crerar, 1993). Once the standard and reference states and concentration scales have been defined for all DC (species) in the α-th phase, it becomes possible to quantify the states of interest, where $C_j < 1$, $a_j \neq C_j$, and $\gamma_j \neq 1$ (or $m_j \neq 1$, $m_j \neq a_j$, and $\gamma_j \neq 1$), and establish conversions from the practical into rational concentration scale. Transformation from the standard state at T_o, P_o to the state of interest at T, P for j-th DC (species) includes four steps (table 3) and results in consistent expressions of prime chemical potentials $\mu_j \equiv \upsilon_j$ for condensed phases, gas mixture and aqueous electrolyte. Based on the Kuhn-Tucker conditions (4), the related expressions for $G(x)_j$ and f_j, f_α have been given by Karpov and others (1997, app. A). Below, these expressions are extended to dependent components (species) of sorption phases, retaining the same notation.

1.2.2. State of interest for the sorbent endmembers.—Specific surface area $A_{\alpha,v}$ and specific surface Gibbs energy of the pure mineral (endmember) in water $\sigma_{j,v}$ are not included into definitions of standard and reference states for the condensed phase endmembers. Hence, the achievement of the state of interest at $A_{\alpha,v} > 0$ and $\sigma_{j,v} > 0$ requires one more step (step 5 in table 3), because large specific surface areas imply small particle/capillary radii which can affect the stability of the sorbent according to the Freundlich-Ostwald equation (eq 20 in Parks, 1990). In the present notation, for the endmember of a congruently- and sparingly soluble mineral, this equation can be written as

$$\ln \frac{K_s}{K_o} = \frac{2k_\alpha \sigma_{j,v} M_{\alpha,v} A_{\alpha,v}}{3RT}$$

where K_o is the intrinsic solubility product; K_s is a surface-perturbed solubility product, and k_α is a factor describing the effect of shape and size distribution of particles ($k_\alpha > 0$) or pores ($k_\alpha < 0$). As only the stability of a mineral but not that of an aqueous species depends on the surface curvature, the difference between K_o and K_s can be attributed to the standard chemical potential of j-th endmember in α-th mineral phase:

$$\mu_j = \frac{g_j^o}{RT} + \frac{\Delta G_{j,s}}{RT} + \ln a_j, \qquad \text{where} \qquad \Delta G_{j,s} = \frac{2}{3} k_\alpha \sigma_{j,v} M_{\alpha,v} A_{\alpha,v}$$

is a molar surface free energy contribution for j-th endmember. Values of $\sigma_{j,v}$ in the range 0.026 to 1.6 $J \cdot m^{-2}$ are known for some common minerals (see table 6.1 in Stumm, 1992), but for many mineral-water interfaces, $\sigma_{j,v}$ are still very uncertain or not available. Moreover, most mineral surfaces are anisotropic and in reality, $\sigma_{j,v,t}$ values must be expected to vary between different faces (indexed with t). Specific surface free energies depend on temperature and, for solid or liquid mixtures, must also change with composition (Adamson, 1990), hence $\sigma_{j,v}$ is referred here to j-th endmember but not the whole solid (which implies that surface free energy of a mixed solid is a weighted average of that for the endmembers).

The surface free energy contribution is often hidden within a measured solubility product K_s (and corresponding g^o value) of a colloidal or thin-particle solid having a large but unknown specific surface area. If this is the case, then one can operationally take $\sigma_{j,v} = 0$, equivalent to an assumption that the stability of the solid is not affected by its surface morphology. Nevertheless, it seems reasonable to consider the surface free energy contribution term $\Delta G_{j,s}$ for theoretical clarity. A complete set of GEM convex programming expressions for a sorbent endmember now can be written:

$$c_j = \frac{g_{j,v}}{RT} + \frac{\Delta G_{j,s}}{RT} + \ln \gamma_j;$$

$$G(x)_j = x_j c_j + x_j \ln \frac{x_j}{X_\alpha};$$

$$\upsilon_j = c_j + \ln \frac{x_j}{X_\alpha} + \Theta_{\alpha,v}; \qquad j \in l_{\alpha,v},\ \alpha \in \Phi;$$

$$f_j = \exp\left(-c_j - \Theta_{\alpha,v} + \sum_{i \in N} a_{ji} u_i \right) - \frac{x_j}{X_\alpha} \leq 0 \tag{6}$$

The above four equations are equivalent to their counterparts for the crystalline solid phase end-members given by Karpov and others (1997), except the two terms: $\Delta G_{j,s}$ (see above) and $\Theta_{\alpha,v}$ which is zero in absence of surface species and is discussed below. As in a condensed phase, the sorbent of sorption phase can be either single-component (for instance, rutile TiO_2) or multi-component [for example, (Mn, Mg, Fe)CO_3 solid solution].

1.2.3. The standard state of a surface species.—In the LMA approach, the surface species are usually considered in the same way as the aqueous complexes, hence the standard state is assumed to be the same as that for solutes in aqueous electrolyte – one mole of surface species per liter or per 1 kg of H_2O, in absence of external fields, that is, at zero surface charge and electrostatic potential $\Psi = 0$ (Davis and Kent, 1990). However, the fixed geometry of surface sites and the charge/potential gradient between the surface and the bulk aqueous phase distinguish surface species from their aqueous counterparts in at least three aspects: (1) surface functional groups cannot be diluted infinitely on the surface (though adsorbed ions can) and must have a fixed density per unit area of the surface monolayer; (2) the proximity of surface sites allows lateral interactions between the surface species; (3) the energy of surface species reflects the complex stereochemical, structural, and electrostatic conditions of the mineral-water interface (Sposito, 1989; Zachara and Westall, 1999). Accordingly, more information has to be fixed in the definitions of standard and reference states for surface species, partially related to the aqueous counterparts, and strongly - to the solid sorbent. Alternative choices are possible, as there is much confusion in the thermodynamic argumentation of SCMs, particularly electrostatic ones involving the Coulombic term $z_j F \Psi/(RT)$, where z_j is a species formula charge, F is Faraday's constant, and Ψ is relative electrostatic potential at the respective surface layer. Absolute values of Ψ cannot be determined; conventionally, $\Psi = 0$ is set for all species in aqueous electrolyte (Adamson, 1990), and the impact of electrostatic interactions is distributed between the G^o values and the activity coefficients of the charged aqueous species. Hence, Ψ will refer here to the potential difference between the EDL plane and the bulk aqueous electrolyte.

In electrostatic SCMs, the Coulombic term is either considered as an activity coefficient (Dzombak and Morel, 1990; Goldberg, 1992) or as a separate part of electrochemical potential of surface species (Sverjensky and Sahai, 1996) – namely, a work contribution due to the presence of an electrostatic field, neither part of the standard chemical potential nor part of the activity term. The former case implies that the reference state (defined as $C_j = a_j$) occurs only at $\Psi = 0$. For neutral surface species (any species in NEM), the Coulombic term is always zero. Does the activity of charged surface species include the Coulombic term correction in the electrostatic SCMs? As noted by Stumm (1992, p. 67), it is impossible to separate the chemical and electrical contribution to the total energy of interaction with a surface without making non-thermodynamic assumptions; the breakdown into a chemical and Coulombic parts is operationally useful. The general form of electrochemical potential, $\mu = \mu^o + \ln C + \ln \gamma + C_F$ (C_F = Coulombic term), suggests that mathematically, C_F makes a correction similar to $\ln \gamma$ (activity coefficient) term, and both must be zero at standard and reference states when (by definition) $\mu = \mu^o$ and the activity term $\ln a = \mu - \mu^o = 0$. The only independent way of finding the numerical value of μ at equilibrium is from the species stoichiometry and chemical potentials of elements and charge (vector u, see Section 1.2). If so, the operational definition of activity, $\ln a = \mu - \mu^o$, must include the Coulombic term for charged surface species in electrostatic SCMs together with the activity coefficient term. The consequence is that, at a fixed total bulk composition of the system, the numerical values of concentrations for a given charged surface species will depend on the choice of EDL model. Hence, it is reasonable to define the standard state of surface species at zero surface charge/potential ($\Psi = 0$) – independent of electrostatic or non-electrostatic site-binding model of the mineral-water interface. There is still no agreement about the "non-electrostatic" activity coefficients of surface complexes, thought to account for the interactions with neighboring surface species; the problem was traditionally circumvented by declaring that these activity coefficients cancel out in the LMA expressions (Davis and Kent, 1990).

Definitions of the standard state for components of the multi-component phases include a standard concentration to which activities and activity coefficients must be scaled (chapter 12 in Anderson and Crerar, 1993). For a given equilibrium state, the (electro)chemical potential of the solute is fixed only by its stoichiometry and total bulk composition of the system, and it is the same whether the concentrations are measured in mole fractions (X), molalities (m), or other units, and what sorts of the activity coefficient- and/or Coulombic corrections are involved. For instance, for the aqueous species,

$$\mu = \mu^o_X + \ln a_X = \mu^o_m + \ln a_m = \mu^o_X + \ln(\gamma_X \cdot X) = \mu^o_m + \ln(\gamma_m \cdot m)$$

where the standard mole fraction concentration is indexed with X and the standard molality – with m. From the above equality and $X = m/(m + 1000/18.0153)$ by definition (18.0153 g is the molar mass of water), one obtains

$$\mu^o_X = \mu^o_m + \ln 55.5084; \ln \gamma_X = \ln \gamma_m + \ln(1 + 0.0180153m)$$

$$\ln a_X = \ln a_m - \ln 55.5084$$

(Anderson and Crerar, 1993, p. 281). From the last equation, it is clear that values of equilibrium constants depend on the chosen standard state concentration scales for all involved species.

In the LMA approach, only product species are provided with thermodynamic data (logK of formation from the master species). Consider, for instance, a reaction $Zn^{+2} + 2Cl^- = ZnCl^o_2$, where zinc and chloride ions are master species, with $\log K = -0.4343\Delta G^o/(RT)$. The Gibbs energy change in this reaction is $\Delta G^o = G^o(ZnCl^o_2) - G^o(Zn^{+2}) - 2G^o(Cl^-)$. Partial molar Gibbs energy G^o of a product species depends on standard molar Gibbs energy of the constituents and on the choice of standard concentration scale. For instance, $G^o_m = G^o_X - 4.016534 \cdot RT$, where $\ln(1000/18.0153) = \ln 55.5084 = 4.016534$. Substitution into the above reaction yields $\Delta G^o_m = \Delta G^o_X + 8.03307 \cdot RT$, and therefore $\log K_m = \log K_X - 3.4887$. In other words, the G^o, ΔG^o, and log K values are sensitive to selection of standard concentration scales, taken to be different for the aqueous, solid and gaseous phase components (Anderson and Crerar, 1993), and commonly assumed for surface species to be the same as that for aqueous species (molar or molal). However, the surface species also belong to the sorbent surface, hence the *specific surface area and site density parameters must be included in the definition of the standard state concentration scale and will affect the* G^o, ΔG^o *and* log K *values for surface complexes* even at otherwise fixed conditions. This important question still remains almost unexplored, although it has already been recognized that the choice of the site density parameter values strongly affects the LMA-fitted values of K^{int} and, hence, the *usage of the same density parameter is necessary* for fitting consistent K^{int} values for various ions and sorbents (Dzombak and Morel, 1990; Davis and Kent, 1990; Hayes and others, 1991).

Suppose that the standard concentration scales have been defined and fixed for all master and product species in the LMA tableau. Then values of ΔG^o and logK for a product species must be constant, and, hence, its partial molar Gibbs energy G^o will depend only on the choice of G^o values for the master species. The latter topic is usually not considered and, in principle, G^o values for master species can be chosen to be any, zero or non-zero, equal or non-equal values, because only logK for the product species is actually used. For gases, minerals, and aqueous ions, however, it is known from thermochemical databases that there must be only one conventional choice when molar G^o values of compounds correspond to $G^o_{elem} = 0$ at standard states of chemical elements at T_o, P_o. Only this choice provides a common reference basis for all G^o values and permits, for instance, the redox state and relative stabilities of all phases in the system to be found from the bulk elemental chemical composition only. Standard thermochemical data are preferential in GEM techniques that need G^o input data for all species of all phases (see sec. 1.2). For the "surface functional group" master species, however, a consistent standard G^o value (at the universal "chemical element standard state" reference level) is yet unknown. It is questionable whether there is any advantage in treating the surface functional group as an independent component with $G^o = 0$.

In $2pK_A$ LMA SCMs, the reactions such as $\equiv OH + Zn^{+2} = \equiv OZn^+ + H^+$ are considered ($\equiv OH$, Zn^{+2} and H^+ taken as the master species). Even if the G^o value of Zn^{+2} ion is taken from a thermochemical database and $G^o(H^+) = 0$ from the standard hydrogen scale convention, log K^{int} of this reaction will depend on the site density parameter of the sorbent, and G^o of $\equiv OZn^+$ will be defined by log K^{int} and the choice of the G^o value for the master species $\equiv OH$. Yet, for the $1pK_A$ SCM reactions that include surface complexes on both sides, but no neutral functional group $\equiv OH$, the situation may be less complicated – at least the increments from site density parameters would divide out from the LMA expression and log K^{int}.

From the above reasoning, one can conclude that the intrinsic adsorption constants K^{int}, fitted using LMA codes at different total site density parameters, most probably refer to different (unknown) standard states and may not be directly correlated. This thesis can be clarified when looking at surface complexation as at an analogue of gas dissolution in water – for instance, in a reaction $O_2(gas) = O_2(aq)$, where a molecular species of fixed stoichiometry leaves one phase for another. Such equilibrium can be described with the Henry constant K_h, which in the case of gas dissolution also includes a molality- to mole-fraction conversion factor. Leaving aside the surface structure and other complications for the moment, let us look at the coordination of an aqueous species Me_{aq} with the sorbent surface in a similar simple way – just as at a process in which the species retains its elemental stoichiometry in transferring from the aqueous phase to the sorption phase. The reaction is then $Me_{aq} = Me_{ads}$ with an equilibrium constant K – that is equal to a ratio of activities at the state of interest and the standard states:

$$K = \frac{a(Me_{ads})}{a^o_{ads}} \cdot \frac{a^o_{aq}}{a(Me_{aq})}$$

The fraction a^o_{aq}/a^o_{ads} will be unity only if the activity of the surface species is expressed in the same concentration scale as that of the aqueous species. But the surface species Me_{ads} belongs to another (sorption) phase, *where its activity at standard state must be scaled by a certain standard molar ratio of surface sites to the whole phase.* Such a ratio would involve the product $\Gamma_C A_{\alpha,v} M_{\alpha,v}$ of the specific surface area $A_{\alpha,v}$, the total site density parameter Γ_C, and the molar mass of the sorbent $M_{\alpha,v}$. Therefore, $a^o_{aq}/a^o_{ads} \neq 1$, and it will vary with Γ_C even at a fixed $X_{\alpha,v}A_{\alpha,v}$ product. This relationship explains why the values of K^{int} should vary with Γ_C value in LMA-fitting of the same titration data set. Abundant evidence for that behavior has indeed been found by Davis and Kent (1990); Hayes and others (1991); Goldberg (1991); Christl and Kretzcshmar (1999).

Continuing the analogy with gas dissolution, one finds another important difference between the "homogeneous" (aqueous, gaseous) and the "heterogeneous" (sorption) phases. The former has no geometrical constraints to the amount of dissolved molecules whose actual concentration is defined by the equilibrium constant and state variables of the system (temperature, pressure). The latter (sorption phase) has a physically (geometrically) fixed number of accessible sites in the surface monolayer – proportional to the amount of surface $A_{\alpha,v}M_{\alpha,v}$ and the *maximum site density* Γ_{max}. This constraint is not important at very low concentrations of Me_{aq} and Me_{ads}, but it has profound consequences at high surface loadings, for a long time recognized in the concept of a *Langmuir isotherm* (Langmuir, 1918; Sposito, 1984). The Γ_{max} parameters, in general, depend on the structure of the mineral-water interface, size and geometry of the adsorbed molecules, and many other factors. Several surface species may exhibit competitive behavior, which implies one common Γ_{max} value. In some systems, especially involving heterogeneous sorption at very low metal concentrations, the cation surface complexes do not seem to compete and must have separate Γ_{max} constraints for attachment to the so-called "strong sites". Hence, due to high individuality and variability of the Γ_{max} limits, it does not seem reasonable to involve them in the definitions of standard and reference states. In fact, there is absolutely no necessity to merge two thermodynamically different parameters - Γ_{max} and Γ_C – into one generic "site density parameter" Γ_T. Unfortunately, this juxtaposition is almost always done in the LMA SCM fitting of potentiometric titration and metal adsorption data, which requires the setting of at least one balance constraint on the total number of moles of surface sites $N_{t,s}$ (= total moles of monodentate surface species), calculated by the user as a product $N_{t,s} = \Gamma_T X_{\alpha,v} A_{\alpha,v} M_{\alpha,v}$. The generic parameter Γ_T is sometimes understood as a Γ_{max} value obtained from crystallographic data (Koretsky and others, 1998) or from experimental measurements such as tritium exchange (Davis and Kent, 1990). When measured data are not available, the value of Γ_T may be guessed, taken as a value recommended in the literature (for instance, 2.31 sites $\cdot$ nm^{-2}, Dzombak and Morel, 1990), or simply treated as a fitting parameter at fixed values of binding constants (Westall, 1995). Because of this confusion, it has not been possible so far to assess the extent of the thermodynamic validity of earlier standard and reference state definitions for surface species inferred for the LMA SCMs. In other words, the site density parameter Γ_T has usually been taken as a blend of two values of different origin - Γ_C and Γ_{max} - and it has not been recognized that the former is part of the standard concentration scale, while the latter refers to surface structure and nature of the surface species on a specific sorbent sample. Thus, a unique combination of the quantity and specific surface area of the bulk sorbent, the aqueous and surface species concentrations, and the total surface (site) density, must be defined and fixed in a thermodynamically rigorous definition of standard state of the surface species.

Keeping in tune with the molal concentration scale for aqueous electrolyte and conventions for the solid species and water-solvent, it is logical to suggest that at the standard state, one mole of a surface species is bound onto surface of one mole of the bulk sorbent suspended in 1 kg of H_2O-solvent at P_o, T in absence of external fields at zero surface potential. Then, any combination of the "standard state" specific surface area $A^o_{\alpha,v}$ (in m$^2 \cdot$ g^{-1}) and the "standard state" total site density Γ_o (in mol $\cdot$ m^{-2}) must obey a constraint

$$A^o_{\alpha,v} M_{\alpha,v} \Gamma_o = 1 \tag{7}$$

Hence, if *one and the same reference value of site density* Γ_o is conventionally fixed to define standard states for monodentate surface species on all sorbents and surfaces, then the *reference specific surface area* $A^o_{\alpha,v}$ (expressed in m$^2 \cdot$ g^{-1} units) will depend only on the molar mass of the sorbent $M_{\alpha,v}$. It is assumed that adsorption occurs within a surface monolayer (Adamson, 1990; Stumm, 1992), which requires that at its standard state, a surface species occupy all sites at a "monolayer" density, in absence of other surface species. It is known (Parks, 1990; Davis and Kent, 1990) that surface (de)protonation on simple oxides such as rutile occurs up to site density around 12 nm^{-2}, which roughly corresponds to the density of a monolayer of water molecules (0.28 nm in diam.). Divided by Avogadro's number, this density is about 20 μmol $\cdot$ m^{-2}. From this simple and realistic consideration, the *reference total surface density* Γ_o is proposed to be taken $2 \cdot 10^{-5}$ mol $\cdot$ m^{-2} $\approx$ 12.05 nm^{-2}, the same for all surface species and all sorbents. From equation (7), a *reference specific surface area* becomes $A_o = A^o_{\alpha,v} M_{\alpha,v} = 1/\Gamma_o = 5 \cdot 10^5$ m$^2 \cdot$ mol^{-1}, also the same for all sorbents. This A_o value can be converted into m$^2 \cdot$ g^{-1} units if molar mass $M_{\alpha,v}$ of the sorbent is known. For instance, molar mass of hydrous ferric oxide (HFO) FeOOH is 89 g $\cdot$ mol^{-1}, so $A^o_{HFO} = 5 \cdot 10^5/89 = 562$ m$^2 \cdot$ g^{-1}, which compares well with 600 m$^2 \cdot$ g^{-1} used by Dzombak and Morel (1990).

The standard state of a surface species is when one mole of it occupies all sites of the reference total density $\Gamma_o = 20\ \mu mol \cdot m^{-2}$ *on a surface of one mole of a sorbent suspended in 1 kg of water-solvent at* P_o *and* T_o*, in absence of external fields and at zero surface potential* $\Psi = 0$*.*

1.2.4. The reference states and activities of surface species.—So far, there has been no clarity in the literature regarding the reference state of surface-bound species. The common idea was that this state should correspond to that assumed for the bulk aqueous solutes, that is, unimolal at a hypothetical infinite dilution (or at constant ionic strength in CCM) and at zero EDL potential (Davis and Kent, 1990). As discussed above, the LMA material balance constraints on the total number of surface functional groups obscured relations between the surface coverage (density) and the reference state of surface species and has not allowed the surface concentration, activity, and activity coefficients to be unambiguously defined. Because the surface species located at the mineral-water interface are "shared" between the bulk sorbent, the water-solvent, and the aqueous ions, the reference state definition should somehow reflect such complex relationships.

Consider a reaction that binds a (neutral) aqueous species M of activity a_{aq} to the mineral surface neutral functional groups S≡ of activity a_n forming a surface species S≡M of activity a_s (in molal scale, charges omitted for simplicity):

$$\begin{array}{ccccc} M & + & S\equiv & = & S\equiv M \\ a_{aq} & & a_n & & a_s \end{array} \tag{8}$$

Let a *maximum expected molal concentration* m_n^o of the non-reacted functional group S≡ be proportional to the product $X_{\alpha,v}M_{\alpha,v}A_{\alpha,v}\Gamma_{max}$, where for the α-th sorbent, $X_{\alpha,v}$ is the number of moles, $M_{\alpha,v}$ is mass per mole, $A_{\alpha,v}$ is specific surface area, and Γ_{max} is a *maximum (site) density parameter,* not necessarily equal to Γ_o (the index for surface types is dropped here for brevity). At very low activity of aqueous species M, that is, close to its reference state, $a_{aq} \approx m_{aq} \rightarrow 0$, and hence for the surface species $a_s \approx m_s \rightarrow 0$. Therefore, practically all the sorbent surface is occupied by the *non-reacted* functional groups (part of them may be *non-reactive* and will never be occupied by sorbates), or $m_n - m_s \rightarrow m_n^o$. Hence, there must be a reciprocal relation between reference states for the surface functional groups (sites) and the surface complexes, similar to that existing for the solutes and the solvent in the bulk aqueous electrolyte. If there is only one surface complex then its reference state is approached on "infinite dilution on the surface" $a_s \approx m_s \rightarrow 0$; at the same time, $a_n \approx m_n^o \cdot \mathrm{const} \rightarrow 1$ correctly approaches another, reciprocal reference state for the non-reacted functional group. In other words, a hypothetical reference state of the surface functional group ($a_n = m_n^o \cdot \mathrm{const} = 1$) can be defined simply when all such groups on the sorbent surface exist at reference density Γ_o and *are free* (non-reacted), and there is one mole of groups on a sorbent with A_o total surface area per 1 kg of H_2O-solvent. The reference state for a surface complex (reacted functional group) occurs at unimolal concentration and (hypothetical) infinitely low surface coverage, corresponding to the infinite dilution reference state of the aqueous counterpart. In this case, the LMA expression of the reaction (8) is:

$$K = \frac{a_s}{a_{aq}} \tag{9}$$

where K is a thermodynamic binding constant. It says that on increasing a_{aq}, m_s will also increase proportionally as $a_s = K \cdot a_{aq}$, as long as most of the surface functional groups remain non-reacted and exist in great excess over the surface complexes, which obviously corresponds to the linear part of the Langmuir isotherm. If the non-reacted surface functional groups belong to the sorbent then their activity must not depend on a_{aq} or a_s, hence $a_n = a_o = \text{const}$. However, the higher the activity a_{aq} of the aqueous counterpart, the more the non-reacted functional groups are consumed to produce surface complexes. This fact makes $m_n < a_n$ and requires the introduction of an "activity coefficient" Ξ_n for the free surface functional groups

$$a_n = m_n \Xi_n, \qquad \Xi_n = \frac{\text{const}}{m_n^o - m_s} \tag{10}$$

assuming that only one surface complex is present. Ξ_n will be called a *free functional group surface activity term*; its derivation for the case of many surface species is given below (sec. 1.3).

Using activity coefficients γ_s for the surface complex and γ_{aq} for the aqueous species, one can rewrite the LMA expression (9) for reaction (8): $K = m_s\gamma_s/(a_n m_{aq}\gamma_{aq})$. The factor γ_s should approach unity at low surface coverage but must increase when concentration of adsorbed species m_s approaches m_n^o, so that upon the further increase of a_{aq} (and $a_s = K \cdot a_{aq}$), $m_s < m_n^o$ is always maintained. This "limiting behavior" is traditionally described by the Langmuir isotherm with a conditional binding constant K_L (Adamson, 1990; Sposito, 1984):

$$m_s = m_n^o \frac{K_L m_{aq}}{1 + K_L m_{aq}} \tag{11}$$

From equations (10) and (11), it must be possible to derive an expression for a *surface species density correction term* γ_s, functionally related to Γ_{max} (see sec. 1.3.1).

It remains further to define a *scaling factor* for the concentrations of surface species at arbitrary values of $X_{\alpha,v}$, $M_{\alpha,v}$, and specific surface area $A_{\alpha,v}$ of the bulk sorbent, in the cases of one or several surface types. This procedure is necessary for determining concentrations and activities of surface species at the state of interest, and connecting them to the standard and reference states. The maximum expected number of moles of a monodentate-bound surface species at the standard state corresponding to a surface monolayer, when this species occupies all the available sites of reference density Γ_o in a t-th surface "patch" (type), is defined as

$$\chi_{\alpha,t}^o = \phi_{\alpha,t} X_{\alpha,v} M_{\alpha,v} A_{\alpha,v} \Gamma_o \tag{12A}$$

and the number of moles of j-th surface species at the state of interest on t-th surface type on α-th sorbent is:

$$x_j = \phi_{\alpha,t} X_{\alpha,v} M_{\alpha,v} A_{\alpha,v} \Gamma_j, \qquad j \in l_{\alpha,s} \tag{12B}$$

where Γ_j is a surface density of j-th surface complex (in $\text{mol} \cdot \text{m}^{-2}$), and $\phi_{\alpha,t}$ is a fraction of total sorbent surface reactive area belonging to t-th surface type. Obviously, at the standard state of the whole sorption phase, $\chi_{\alpha,t}^o = 1$ mol; $X_{\alpha,v} = 1$ mol; $\phi_{\alpha,t} = 1$, and $A_{\alpha,v}^o M_{\alpha,v} \Gamma_o = 1$ ($\Gamma_o = 2 \cdot 10^{-5}\ \text{mol} \cdot \text{m}^{-2}$). To express concentrations and activities of surface species in the molal scale, $\chi_{\alpha,t}^o$, x_j, and a_j must be multiplied by a factor $55.5084/x_w$ where x_w is the number of moles of water-solvent in the system. By definition, activity and concentration at the state of interest must be scaled to the standard-state concentration. Therefore, in the molality scale,

$$m_j = (55.5084/x_w \cdot x_j)/(55.5084/x_w \cdot \chi_{\alpha,t}^o) = x_j/\chi_{\alpha,t}^o = C_j \tag{12C}$$

where $\chi_{\alpha,t}^o$ is defined from (eq 12A); substituting (eq 12A) into (eq 12C), one obtains

$$C_j = x_j/(\phi_{\alpha,t}X_{\alpha,v}M_{\alpha,v}A_{\alpha,v}\Gamma_o) \tag{12D}$$

Alternatively, using equation (7) to express Γ_o, the sorbent molar mass and Γ_o can be eliminated:

$$C_j = x_jA^o_{\alpha,v}/(\phi_{\alpha,t}X_{\alpha,v}A_{\alpha,v}) \tag{12E}$$

Substitution of (eq 12B) into (eq 12D) yields

$$C_j = \Gamma_j/\Gamma_o \tag{12F}$$

The last equation shows that the concentration of a surface- bound species, as defined here, is a ratio of its current density Γ_j to the reference density Γ_o, numerically equal to the monolayer surface-type mole fraction $x_j/\chi^o_{\alpha,t}$ (eq 12C). The important point here is that the Γ_j/Γ_o parameter is not the same as the *fractional surface coverage* $\theta = \Gamma_j/\Gamma_{max}$ commonly considered in surface chemistry (Adamson, 1990) in relation to the Langmuir isotherm. The difference is that constant Γ_o is set conventionally to be the same for all mineral-water interfaces and serves in (eq 12F) for scaling to the standard-state surface concentration, while the Γ_{max} parameter determines a "geometrical" limit of adsorption on a specific sample surface and varies strongly between minerals and surfaces. In other words, Γ_o is a thermodynamic quantity (part of the definition of the standard state), while Γ_{max} is a physical, non-thermodynamic value that must be attributed to the "surface activity coefficient" corrections only.

The surface density fraction defined as Γ_j/Γ_o (or monolayer mole fraction $x_j/\chi^o_{\alpha,t}$) is invariant to the amount and specific surface of the sorbent and to quantities of other (aqueous, gaseous, solid) phases in the system. Equation (12E) connects the number of moles x_j of surface species with the amount $X_{\alpha,v}$ of the sorbent and the properties of its surfaces ($A^o_{\alpha,v}$, $A_{\alpha,v}$, $\phi_{\alpha,t}$). Introducing two activity coefficients γ_j ("geometrical", related to Langmuirian behavior) and λ_j (reserved for the description of other physical effects such as the lateral and long-range interactions on surfaces), the activity of the j-th surface species (at zero surface potential) can be expressed as:

$$a_j = \frac{\Gamma_j}{\Gamma_o}\lambda_j\gamma_j = \frac{A^o_{\alpha,v}x_j}{\phi_{\alpha,t}A_{\alpha,v}X_{\alpha,v}}\Xi_j \tag{13}$$

At a later stage, we will not differentiate between the two kinds of activity coefficients, hence their product $\Xi_j = \lambda_j\gamma_j$ is called a *surface activity (correction) term* (SAT). More precise description of the surface activity corrections has to be left for future studies; only the "geometrical" SAT will be considered below in its simplest form for monodentate surface binding (sec. 1.3).

1.2.5. State of interest of the surface species (a multi-surface-site formulation).—According to the definition of the electrochemical potential (Adamson, 1990), $\mu =; \mu^o + \ln a + C_F$ (C_F = Coulombic factor) and using (eq 13) for the activity a, the full expression of (electro)chemical potential of a j-th monodentately-bound surface species can now be written:

$$\mu_j \equiv \upsilon_j = \frac{g_{j,T,P}}{RT} + 4.016534 + \ln\frac{A^o_{\alpha,v}}{\phi_{\alpha,t}A_{\alpha,v}} + \ln\frac{x_j}{X_{\alpha,v}} + \ln\Xi_j + \frac{F}{RT}z_j\Psi_{\alpha,t} \tag{14}$$

where z_j is the effective formula charge, F is Faraday's constant, $\Psi_{\alpha,t}$ is a relative electrostatic potential on t-th surface type (at the appropriate EDL plane), R is the universal gas constant, and $4.016534 = \ln(1000/18.0153)$ provides the conversion from the molal concentration scale, in which $g_{j,T,P}$ is taken. The $g_{j,T,P}$ stands here for the partial molal Gibbs energy at the temperature and pressure of interest, related to a thermodynamic equilibrium constant K_j. The right-hand side of (eq 14) is arranged into six terms instead of three ($\mu^o + \ln a + C_F$) to facilitate an understanding of the factors influencing the stability of surface species. There are several useful features of equations (13) and (14):

1. The activity of a surface species is auto-scaled to the bulk amount of sorbent $X_{\alpha,v}$, its specific surface area $A_{\alpha,v}$, and fraction of this area related to a surface type $\phi_{\alpha,t}$.

2. The Coulombic term C_F is separated from the SAT $\ln \Xi_j$ and $g_{j,T,P}$ terms, which makes the two latter values applicable to any site-binding thermodynamic model and comparable for TLM, DLM, and NEM[1].

3. The standard molal Gibbs energy functions of surface species $g_{j,T,P}$ depend only on the reference specific surface area $A^o_{\alpha,v}$ (equivalently, on the reference density Γ_o), but not on any particular maximum (site) density values $\Gamma_{j,max}$, which makes the $g_{j,T,P}$ (and respective K_j) values of surface species comparable between all mineral oxide surfaces and sorbents.

4. The dependence of activity, concentration, and (electro)chemical potential of the surface species on $\Gamma_{j,max}$ is described only by the SAT $\ln \Xi_j = f(\Gamma_j, \Gamma_{max}) \geq 0$. At low Γ_j, $\Xi_j = 1$ and adsorption occurs in the *region of geometrically ideal SCM behavior* for j-th surface species, proportional to the activity of the aqueous counterpart (in the case of electrostatic SCM, this is true for neutral surface species only). At higher coverage $\theta_j \rightarrow 1$ ($\Gamma_j \rightarrow \Gamma_{j,max}$), $\Xi_j >> 1$ and adsorption occurs in the region of geometrically non-ideal SCM behavior, where Γ_j and x_j become asymptotically independent of the activity of the aqueous sorbate.

5. If the stoichiometry of a surface species is defined only using chemical elements and charge then (eq 14) permits the standard $g_{j,T,P}$ and ambient-temperature G^o_j values for surface species to be found which are fully consistent with those for aqueous species, solids and gases from the thermodynamic database. Moreover, if the stoichiometry of the sorbent is not included into the formulae of surface species, their standard partial molal properties become comparable between different mineral-water interfaces.

It follows from (eq 14) that transformation from the standard and reference states to the actual state of interest for a surface species consists of several steps listed in table 4. This sequence clearly reflects the "interfacial" nature of surface species, whose molalities depend on the amount and properties of the bulk sorbent, maximum density parameters, composition of aqueous phase, and the EDL charge.

1.2.6. The convex-programming expressions for surface species.—Re-arrangement of (eqs 6) using (eq 14) yields a set of expressions summarizing the properties of a surface species on a sorption phase in the convex programming approach:

$$c_j = \frac{g_{j,T,P}}{RT} + 4.016534 + \ln \frac{A^o_{\alpha,v}}{\phi_{\alpha,t} A_{\alpha,v}} + \ln \Xi_j + \frac{F}{RT} z_j \Psi_{\alpha,t}, \qquad j \in l_{\alpha,s};$$

$$G(x)_j = x_j c_j + x_j \ln \frac{x_j}{X_{\alpha,v}}, \qquad j \in l_{\alpha,s}, \qquad \alpha \in \Phi_s;$$

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

$$f_j = \exp\left(-c_j + \ln \frac{X_{\alpha,v}}{X_\alpha} - \Theta_{\alpha,s} + \sum_{i \in N} a_{ji} u_i \right) - \frac{x_j}{X_\alpha} \leq 0, \qquad (15)$$

---

[1] CCM is defined at different reference state of aqueous solution ("constant ionic strength") and, for this reason, is not considered here.

TABLE 4

Transformations from standard states to states of interest for the surface species

#	Step	Description
1	From P_o, T_o to P, T of interest	Calculation of partial molal Gibbs energy $g_{j,T,P}$
2	From reference A_o to arbitrary $A_{\alpha,v}$ specific surface area	Addition of $-\ln(A_{\alpha,v}M_{\alpha,v}\Gamma_o)$ to $\mu^o_{j,T} = g_{j,T,P}/(RT)$
3	From a single surface to t-th surface type on the sorbent	Addition of $-\ln \phi_{\alpha,t}$
4	From 1 mole to arbitrary quantity of the sorbent $X_{\alpha,v}$	Addition of $-\ln X_{\alpha,v}$
5	From standard (1 mole) to arbitrary quantity of sorbate x_j	Addition of $\ln x_j$
6	From reference (ideal) to the geometrically non-ideal state	Addition of SAT $\ln \Xi_j = f(\Gamma_j, \Gamma_{max}) \geq 0$
7	Elecrostatic SCM correction	Addition of the Coulombic term (at $\Psi_{\alpha,t} \neq 0$, $z_j \neq 0$)
8	From practical to rational scale of concentrations	Molality - to mole-fraction conversion (addition of ln55.51 and non-logarithmic terms)

Note: Steps 2 to 7 convert from the standard activity a_o to the actual concentration.

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

$$\Theta_{\alpha,s} = 1 - \frac{X_{\alpha,v}}{X_\alpha} - \frac{\theta_0}{1+\theta_0}, \qquad \text{where} \qquad \theta_0 = A_{\alpha,v}M_{\alpha,v}\Gamma_o \tag{16}$$

The respective asymmetry correction term for the sorbent (see eqs 6) is

$$\Theta_{\alpha,v} = 2 - \frac{X_\alpha}{X_{\alpha,v}} - \frac{X_{\alpha,v}}{X_\alpha} + \theta_0 - \frac{\theta_0}{1+\theta_0} \tag{17}$$

Both asymmetry correction terms are important for obtaining a feasible initial approximation and for efficient numerical convergence of the IPM non-linear minimization algorithm. These terms actually compare the current (variable on iterations) mole fraction of the bulk sorbent to that prescribed from $A_{\alpha,v}\Gamma_o$, and tend to compensate each other close to G(x) minimum (assuming that the $\equiv OH^o$ species is included). They are mathematically equivalent to the respective non-logarithmic terms for aqueous solutes and water-solvent, first found by Karpov by explicit differentiation of the $G(x)_\alpha$ increment for an asymmetric phase. The mathematical form of (eqs 15) is similar to that for the aqueous species (Karpov and others, 1997). Summation of $G(x)_j$ and f_j over the whole phase (sorbent + surface species) results in equations of exactly the same form as the expressions for aqueous and other "usual" phases in convex programming formulation (Φ_s denotes a set of sorption phases):

$$G(x)_\alpha = \sum_{j \in l_\alpha} x_j c_j + \sum_{j \in l_\alpha} x_j \ln \frac{x_j}{X_\alpha} - \sum_{j \in l_{\alpha,s}} x_j \ln \frac{X_{\alpha,v}}{X_\alpha}, \qquad \alpha \in \Phi_s$$

$$f_\alpha = \sum_{j \in l_{\alpha,v}} f_j + \sum_{j \in l_{\alpha,s}} f_j - 1 \le 0; \qquad \sum_{j \in l_{\alpha,v}} \Theta_j + \sum_{j \in l_{\alpha,s}} \Theta_j = 0 \qquad (18)$$

This fact permits direct usage of the IPM algorithm for the calculation of equilibria in the systems involving any number of sorption phases. Some extensions had to be made by the author only to the data structures and subroutines for calculation of SAT and c_j terms for multiple surface types. Currently, the TLM (following Hayes and others, 1991), the DLM (following Dzombak and Morel, 1990), and the NEM (non-electrostatic site-binding model) can be applied at 1 to 6 surface types per sorption phase. All necessary computations have been implemented in GEM-Selektor codes (http://les.web.psi.ch/Software/GEMS-PSI).

1.3. Surface Activity Terms Related to Maximum Density Parameters

In the LMA SCMs, the total number of reactive surface sites of *t*-th type is always fixed by an additional mass balance constraint (Morel and Hering, 1993; Zachara and Westall, 1999):

$$N_{t,s} = A_T \Gamma_T \qquad (19)$$

where A_T is the total surface area (m^2), and Γ_T is the t-th total site density parameter ($mol \cdot m^{-2}$) for the surface type. This fact is not very convenient for the multi-site sorption models, because several $N_{t,s}$ values must be *a priori* fixed and supplied as input data (that is, mass-balance constraints).

In GEM thermodynamic formulation, constraints such as $N_{t,s}$ can be avoided and replaced by the SAT Ξ_s aimed at suppressing the concentration of j-th surface complex when, upon increasing activity of the aqueous sorbate counterpart, its actual density Γ_j approaches a physical limit defined by a maximum density parameter Γ_{max}. The limiting value $\Gamma_{t,max}$ may either be the same for all species competing on a t-th surface type (*competitive adsorption*), or several site types, selective for certain sorbates, may co-exist on a surface type, each with its own value of $\Gamma_{j,max}$ (*non-competitive adsorption*). Together, these two options create a new modeling tool for even complex cases of sorption heterogeneity, such as Mn oxides or clays (Kulik and Kersten, 1998; Kulik and others, 2000a).

In the GEM notation, the reference density Γ_o is used only for normalization to the standard state and it is *not the same* as the maximum (site) density parameter, specific either for a surface type ($\Gamma_{t,max}$) or for a single surface species ($\Gamma_{j,max}$). To the author's knowledge, this distinction has never been done in the LMA models, where one value Γ_T (setting an obsolete balance constraint, eq 19) is actually treated both as the maximum density Γ_{max} and as a *conditional total site density* Γ_C to which the fitted values of the 2pK_A intrinsic adsorption constants K^{int} refer. As shown elsewhere (Kulik and Peretyashko, 1998; *ms* in preparation), the values of K^{int} fitted at different total site density parameters $\Gamma_{C1} \neq \Gamma_{C2}$ are not directly comparable. They must be converted to the same reference site density Γ_o *before making any attempts to compare or correlate them,* even for surfaces of the same mineral.

In the GEM theoretical context, the approximate conversion of adsorption constants from the conditional Γ_C to the reference density Γ_o becomes rather simple. Let $\Gamma_o = q \cdot \Gamma_C$ with a constant multiplier $q \neq 1$ and substitute $q \cdot \Gamma_C$ instead of Γ_o into (eq 13):

$$a_j = \frac{\Gamma_j}{\Gamma_o} \Xi_j = \frac{1}{q} \frac{\Gamma_j}{\Gamma_C} \Xi_j, \qquad \text{or} \qquad a_j^{(0)} q = a_j^{(C)} \qquad (20)$$

Further substitution using (eq 9) yields $K_j^{(0)}q = K_j^C$ because the activity of a not-yet-reacted neutral surface functional group is constant (see sec. 1.3.3). Assuming that the reaction for K is written with a neutral functional group on the left-hand side and the surface complex on the right-hand side (for instance, $\equiv OH^o = \equiv O^- + H^+_{aq}$), the conversion into a logarithmic scale yields:

$$\log K_j^{(o)} = \log K_j^C + \log \frac{\Gamma_C}{\Gamma_o} \tag{21}$$

If the neutral functional group stays on the right-hand side of the reaction, the sign at the last term of (eq 21) must be inverted. For example, Dzombak and Morel (1990) fitted intrinsic DLM constants for "weak" metal surface complexes on hydrous ferric oxide at $\Gamma_{C1} = 2.254$ nm^{-2} and for "strong" surface complexes – at $\Gamma_{C2} = 0.056$ nm^{-2}. It follows from (eq 21) that the conversion of log K^{int} to log K at a reference site density $\Gamma_o = 12.05$ nm^{-2} requires addition of $\log(2.254/12.05) \approx -0.73$ for "weak" surface complexes and $\log(0.056/12.05) \approx -2.33$ for "strong" complexes. These examples give an idea about the uncertainty that may be introduced into correlation/prediction of log K^{int} by fitting experimental data at different total site densities for various mineral surfaces, if no conversion to the same conventional reference site density Γ_o has been performed (for instance, as it took place in the correlations by Sahai and Sverjensky, 1997a,b).

1.3.1. SAT for non-competitive adsorption.—To derive equations for the iterative calculation of SAT Ξ_j in GEM, let us recall equations (7) to (12) first for the simple case of non-competitive monodentate adsorption. Assume exactly 1 kg of water-solvent in the system, which makes molalities m_j numerically equal to number of moles x_j for aqueous and surface species. The maximum possible amount of a surface complex can now be defined as an *expected limiting number of moles* $\chi_{j,t,L}$ of j-th species on t-th surface type:

$$\chi_{j,t,L} = \phi_{\alpha,t} A_{\alpha,v} X_{\alpha,v} M_{\alpha,v} \Gamma_{j,t,max} \tag{22}$$

Here, $\phi_{\alpha,t}$, $A_{\alpha,v}$, $\Gamma_{j,t,max}$ are input constants, and $X_{\alpha,v}M_{\alpha,v}$ may, in principle, vary slightly according to the equilibration in the whole system. As the j-th sorbate accumulates on the surface, the SAT must suppress x_j to satisfy the physical constraint $x_j < \chi_{j,t,L}$. This behavior actually goes back to the classic idea of the Langmuir isotherm (eq 11). Let, for simplicity, $\Psi = 0$ and the elemental stoichiometry of a surface species be the same as that of its aqueous counterpart (sorbate). Chemical potentials of both species are then equal ($\mu_s = \mu_{aq}$) and $\mu_n = 0$ at equilibrium, so that (eq 8) simplifies to

$$M_{aq} = M_s \tag{23}$$

- analogous to an interphase-transfer reaction with an equilibrium constant:

$$\ln K = \ln a_s - \ln a_{aq} \tag{24}$$

At low surface coverage ($a_s \approx C_s$), approximately, $\ln a_s = \ln a_{aq} + \ln K$ and thus

$$\ln C_s + \ln \Xi_s = \ln m_{aq} + \ln \gamma_{aq} + \ln K \tag{25}$$

where C_s is the concentration of surface species. Recalling (eqs 12D and 22), the current C_s and the limiting C_L concentrations of surface species become (j and α indices dropped for brevity):

$$C_s = x_s/(\phi_t X_v M_v A_v \Gamma_o) \tag{26A}$$

$$C_L = \chi_L/(\phi_t X_v M_v A_v \Gamma_o) \tag{26B}$$

Note that both concentrations are normalized to the reference density Γ_o but not to the maximum site density $\Gamma_{s,max} = \Gamma_{j,t,max}$. As follows from equation (22), the maximum density parameter is involved only in the "Langmuirian" limiting number of moles χ_L but not in C_s scaling factors.

As long as $C_s << C_L$, any increase in a_{aq} will result in a proportional increase of $C_s = K \cdot a_{aq}$, thus $a_s \approx C_s$ and, hence, $\Xi_s \approx 1$. In this "geometrically linear" adsorption region, described by a "Henrian" slope, the SAT correction is obsolete, and $\Xi_s = 1$ is required. However, during a further increase of the aqueous sorbate activity, the expression $a_s = K \cdot a_{aq}$ still holds, but upon $C_s \rightarrow C_L$, $C_s < C_L$ must also hold because χ_L is *physically* limited by the maximum density $\Gamma_{s,max}$ of sites available for this surface species (eq 22). Keeping in mind that, by definition, $\ln a_s = \ln C_s + \ln \Xi_s$, the simplest way to ensure the above requirements at an arbitrary increase of a_{aq} and a_s is to express the surface activity term as $\Xi_s = C_s/(C_L - C_s)$, or

$$\ln \Xi_s = \ln C_s - \ln (C_L - C_s) \tag{27A}$$

$$\ln \Xi_s = \ln K + \ln a_{aq} - \ln C_s \tag{27B}$$

At given values of C_L, K, and a_{aq}, the system (eqs 27A and 27B) with two unknowns C_s and Ξ_s can be solved to find the concentration of the surface species C_s and the SAT value Ξ_s. A condition $\ln \Xi_s \geq 0$ ($\Xi_s \geq 1$) must be taken into account because the SAT correction is not necessary at low surface loadings $\Gamma_s << \Gamma_{s,max}$ (or $C_s << C_L$), where adsorption is assumed to be linear. Therefore, equation (27A) is only applicable at $C_s > \text{const} \cdot \frac{1}{2} C_L$.

The SAT function $\Xi_s = C_s/(C_L - C_s)$ can reach large values if the equilibrium concentration of the surface species C_s approaches closely to the limiting concentration C_L. In this sense, Ξ_s may behave mathematically stiff and requires some care to be taken when it is calculated among the iterations of the numerical equilibrium solvers. By dividing the numerator and the denominator by C_L, the SAT function can be converted into a familiar (Adamson, 1990) Langmuirian factor

$$\frac{\theta}{1-\theta} \quad \text{where} \quad \theta = \frac{C_s}{C_L} = \frac{\Gamma_s}{\Gamma_{s,max}} \text{ is a \textit{fractional surface coverage}, } 0 < \theta < 1.$$

Alternatively, using equations (26A and 26B) and re-arranging, the SAT function Ξ_s can be expressed as a mole ratio:

$$\Xi_s = \frac{x_s}{\chi_L - x_s} \quad \text{or} \quad \ln \Xi_s = \ln x_s - \ln (\chi_L - x_s) \tag{28}$$

Conversion to molalities is straightforward, resulting in $\ln \Xi_s = \ln m_s - \ln(m_L - m_s)$. Equation (28) was preferred for calculation of the SATs on iterations of the GEM IPM algorithm. Returning to the full GEM notation, the simplest equation for a *non-competitive surface activity term* (SAT), based on the assumption that $\Xi_s = 1$ along the linear part of adsorption isotherm, becomes:

$$\ln \Xi_j^{(n)} = \begin{cases} 0, \ x_j \leq \frac{1}{2} \chi_{j,t,L}; \\ \ln x_j - \ln (\chi_{j,t,L} - x_j) \end{cases} \tag{29}$$

Calculated automatically together with activity coefficients at the GEM IPM algorithm iterations, (eq 29) reproduces shapes of the Langmuir isotherm with the linear part (according to eq 24) at low surface coverage $\Gamma_j \leq 0.5\Gamma_{j,t,max}$, then bending asymptotically to $\Gamma_{j,t,max}$ at higher coverage. The actual $\Gamma_{j,t,max}$ input value is a non-thermodynamic parameter and must be provided, at best, from the independent sample characterization using spectroscopic, high-resolution microscopic, or crystallographic techniques. If $\Gamma_{j,t,max}$ value is unknown, it can also be treated as a fitting parameter; as a zero approximation, $\Gamma_{j,t,max} = \Gamma_o$ can be assumed. This (non-competitive) form of SAT permits us to assign *separate maximum densities to reactive sites of different energy on the same surface without introducing the total site balance constraints,* and enables GEM technique to model multi-site sorption when sorbates do not compete for sites of the same type.

1.3.2. SAT for competitive adsorption.—If several sorbates compete for sites on the same surface type then their *total* must not exceed the expected number of moles defined by the limiting density of such sites $\Gamma_{t,L,max}$:

$$X_{\alpha,t,L} = \phi_{\alpha,t} A_{\alpha,v} X_{\alpha,v} M_{\alpha,v} \Gamma_{t,L,max} \tag{30}$$

Each of the competing species must obey a constraint

$$x_j < \chi_{t,L} \qquad \text{where} \qquad \chi_{t,L} = X_{\alpha,t,L} - \sum_{k \in l_a^{(r)}} x_k, \qquad j \in l_\alpha \backslash l_{\alpha,n}; \qquad k \neq j \tag{31}$$

and $l_{\alpha,n}$ stands for a set of non-reacted functional groups which, if included into the model, require a special form of SAT correction (sec. 1.3.3). Now, $\chi_{t,L}$ is the quantity of sites not yet occupied by any of the competing sorbates. A *competitive surface activity term* can be defined as:

$$\ln \Xi_j^{(c)} = \begin{cases} 0, \; x_j \leq \frac{1}{2} \chi_{t,L}; \\ \ln x_j - \ln (\chi_{t,L} - x_j) \end{cases} \tag{32}$$

Evidently, both competitive and non-competitive species can be considered on the same surface; in this case, the non-competitive "strong" surface complexes must also be included into summation where $\chi_{t,L}$ is calculated. The analogy to the "competitive" form of the Langmuir isotherm (Adamson, 1990; Sposito, 1984) is obvious. As in the case of the non-competitive SAT, the $\Gamma_{t,L,max}$ is a non-thermodynamic value and must be provided as an input value from independent micro/spectroscopic, crystallographic data, measurements of maximum adsorption, or, alternatively, obtained as a fitting parameter from titration data for a multi-sorbate system.

1.3.3. SAT for non-reacted surface sites.—Numerical tests have shown that the GEM-modeled titration curves for single- or multiple-site SCMs are the same, regardless of whether or not the "non-reacted" neutral ≡OH functional group is included as one of the surface species. This finding supports our assumption (eq 10) that the activity of the free functional group does not depend on the concentration of solutes in the bulk electrolyte and on the actual density of "reacted" sites. Imagine that all the neutral functional groups are non-reactive on a hydrated mineral surface. Then there will be no other surface species, hence (see eq 13) $\Gamma_{jn} = \Gamma_o$, $a_{jn} = 1$ (in mole fraction scale), and $\Xi_{jn} = 1$ (the jn index refers to the non-reacted functional group).

Assuming that neutral functional groups on the surface are H_2O molecules from the adsorbed water monolayer, one can make a step forward by setting conventionally

$$\ln a_{jn} = \ln a_w + \ln 55.5084 \tag{33A}$$

where a_{jn} is taken in the molal scale and $a_w \leq 1$ in mole fraction scale is the activity of liquid water in the system, close to 1 in diluted aqueous electrolytes. Equation (13) then yields

$$\ln a_{jn} = \ln \frac{x_{jn}}{X_{\alpha,v}} + \ln \frac{A^o_{\alpha,v}}{\phi_{\alpha,t} A_{\alpha,v}} + \ln \Xi_{jn} = \ln a_w + \ln 55.5084 \tag{33B}$$

in mole fraction scale. From (eqs 33B, 12D, and 12E), at $\Xi_{jn} = 1$, one can calculate the number of moles x_{jn} of neutral non-reacted functional groups on t-th surface type of α-th sorption phase:

$$\ln x_{jn} = \ln a_w + \ln 55.5084 + \ln (\phi_{\alpha,t} A_{\alpha,v} M_{\alpha,v} X_{\alpha,v} \Gamma_o) \qquad (33C)$$

The first consequence of equations (33A, B, and C) is that the neutral surface functional groups on the mineral-water interface must have the same activity on all surface types and, hence, such groups are *macroscopically indistinguishable* before they will react with aqueous sorbates to yield surface complexes. In other words, the *different reactivity of surface sites reveals itself only in the energetics of adsorption reactions, thermodynamic properties of surface complexes, and their maximum densities.* There is nothing weird in the above statement, if one views the neutral functional group as a "surface monolayer solvent." In an aqueous electrolyte, water-solvent provides a medium for solvation of ions, formation of hydroxocomplexes, et cetera, but all the H_2O molecules are thermodynamically the same, only products of their reactions with ions are stoichiometrically and energetically different.

The second consequence is that, again similar to H_2O solvent in the bulk electrolyte, the neutral functional groups must retain practically constant activity ($\ln a_{jn} \approx 4$ in molal scale) regardless of many orders-of-magnitude changes in the concentrations and activities of sorbates (aqueous H^+, OH^-, and other ions) and surface complexes that take place in the experimental titrations. Therefore, the "surface monolayer solvent" species cannot compete with sorbates; rather, the functional groups give up the surface sites to form surface complexes, that is, *yield* to increasing concentration of aqueous sorbates binding to the surface. To some extent, this asymmetry is reflected in the reciprocal definitions of reference states (sec. 1.2.4). On the buildup of the surface complexes, they deviate from the "infinite surface dilution" state and, at the same time, the surface functional groups deviate from the "full surface coverage at reference density" state toward the state of interest. Hence, this "give-up" behavior of the functional groups must be accounted for by using an activity coefficient because their activity a_{jn} is (almost) constant, but surface concentration (density) strongly decreases upon the formation of surface complexes.

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 $a_w \approx 1$, equation (33C) can be rewritten as:

$$\ln x_{jn} \approx \ln 55.51 + \ln (\phi_{\alpha,t} A_{\alpha,v} M_{\alpha,v} X_{\alpha,v} \Gamma_o) - \ln \Xi_{jn}; \qquad \Xi_{jn} = \Gamma_o / \Gamma_{t,max} \qquad (33D)$$

The surface activity term Ξ_{jn} now represents a constant contribution to chemical potential of the neutral functional group, due to the constant input $\Gamma_{t.max}$ parameter (compare with eq 20 describing impact of a change in total site density on activity of a surface complex). Variable part of the SAT must reflect the "give-up" behavior of functional groups upon formation of surface complexes. Let

$$\Omega_{\alpha,t} = \sum_{k \in l^{(r)}_{\alpha,t}} x_k; \qquad k \neq jn \qquad (34)$$

stand for a total number of moles of surface complexes on t-th surface type of α-th phase, and

$$\chi_{tn,max} = \phi_{\alpha,t} A_{\alpha,v} M_{\alpha,v} X_{\alpha,v} \Gamma_{t,max} - \Omega_{\alpha,t} \qquad (35)$$

be an expected number of moles of functional groups that remain 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 $\Xi_{jn} \Rightarrow \Gamma_o/\Gamma_{t,max}$, or $x_{jn} \Rightarrow \chi^o_{tn,max} \Rightarrow \phi_{\alpha,t}A_{\alpha,v}M_{\alpha,v}X_{\alpha,v}\Gamma_{t,max}$. As the progress of adsorption creates more and more surface complexes, $\Omega_{\alpha,t}$ increases, and (as follows from eq 34), ln Ξ_{jn} must become more positive to keep x_{jn} close to $\chi_{tn,max}$. In the extreme case, practically all sites are occupied by surface complexes, that is, $x_{jn} \Rightarrow 0$, $\chi_{tn,max} \Rightarrow 0$, and $\Omega_{\alpha,t} \Rightarrow \phi_{\alpha,t}A_{\alpha,v}M_{\alpha,v}X_{\alpha,v}\Gamma_{t,max}$ and all the non-reacted functional groups are eliminated (for instance, as assumed for ion exchange on permanent-charge surfaces or in $1pK_A$ SCMs). Such behavior at both limits can be described using a complete SAT function:

$$\Xi_{jn} = \frac{\Gamma_o}{\Gamma_{t,max}} \cdot \frac{x_{jn}}{\chi_{tn,max}} \qquad (36)$$

Equation (36) 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 no need to include the non-reacted functional group in GEM SCM modeling runs. Although numerical calculations involving (eq 36) are of theoretical interest only, they do help in interpretation of K^{int} values fitted using the LMA speciation codes.

1.3.4. Some remarks about the nature of SAT.—Equations (29) and (32) describe the simplest case of "geometrically non-ideal" behavior of surface species bound to the available sites of physically limited density in the surface monolayer. The mathematical form of the SAT equations is very similar to the Langmuir isotherm, which results from a model of monodentate attachment of a single adsorbate onto a single adsorbent with fixed number of adsorption sites all with an equal free energy of adsorption at a fixed temperature ("single-site" adsorption). It is usually assumed (Banwart, 1997) that the Langmuir isotherm produces a "linear" part, $C_s = K_d C_{aq}$, at small fractional surface coverage $\theta << 1$, and a non-linear part, $\theta/(1 - \theta) = C_s/(C_L - C_s) = K_d C_{aq}$, at high surface coverage $\theta \rightarrow 1$ (K_d is a distribution coefficient). Recalling equations (25) and (27A), an equilibrium concentration C_s of a surface complex can be expressed as

$$C_s = \frac{a_s}{\Xi_s} = K \cdot a_{aq} \frac{C_L - C_s}{C_s} = K \cdot m_{aq}\gamma_{aq} \frac{1 - \theta}{\theta}$$

From this equation, the linear part of the Langmuir isotherm (ignoring the aqueous sorbate activity coefficient γ_{aq}) follows immediately if $\theta/(1 - \theta) = 1$. This relationship is possible only at $\theta = 0.5$ (or $C_s = 0.5C_L$). However, at any $\theta < 0.5$, $\theta/(1 - \theta) < 1$ and at $\theta \rightarrow 0$, $\theta/(1 - \theta) \rightarrow 0$. Hence, the Langmuir isotherm contains a "geometrical" activity coefficient $\Xi_s = \theta/(1 - \theta)$ accounting for non-ideal adsorption behavior at $\theta \rightarrow 1$, but truncated to $\Xi_s \geq 1$ to ensure the linear relationship $C_s = K \cdot a_{aq}$ at $\theta < 0.5$. This coefficient is applied to the SAT equations (29) and (32). As seen from the numerical examples (pt. 3), these SAT equations are efficient and quite satisfactory, at least as a first-order approximation. Note that truncation of SAT to $\Xi_s \geq 1$ has no theoretical justification - it is applied as a first step toward a deeper understanding of the adsorption non-ideality in the geometrical sense. Other SAT corrections likely will be required to describe polydentate binding or to describe cases of strong lateral interactions between surface complexes.

PART 2. STOICHIOMETRY AND THERMODYNAMIC PROPERTIES OF SURFACE SPECIES ON OXIDE-WATER INTERFACES

Unlike the LMA techniques, the GEM algorithms cannot utilize the reaction stability constants and require as input data the elemental stoichiometries and values of standard partial molal Gibbs energy G^o_j, consistent for all species included in all phases which potentially can appear in the equilibrium state. Other standard partial molal properties (entropy S_j^o, enthalpy H_j^o, heat capacity Cp_j^o, volume V_j^o) of the species must be known for calculations of the molal Gibbs energy function $g_{j,T,P}$ at the T, P of interest different from the reference $T_o = 25°C$, $P_o = 1$ bar. However, contrary to that for minerals, gases and aqueous species, consistent standard partial molal properties of surface species were generally not known up until now because of some confusion in the definitions of standard and reference states. This work presents the derivation of consistent G_j^o values for surface species (in $2pK_A$ SCMs) on amphoteric oxide surfaces (such as rutile or silica) at ambient conditions. Extension to hydrothermal conditions is straightforward and is given elsewhere (Kulik, 2000).

2.1. Selection of Thermodynamic Data

For gases and many minerals, thermochemical properties have been measured or estimated, and collected in several internally consistent databases (Nordstrom and Muñoz, 1994; Langmuir, 1997, and references therein). A comprehensive data set for aqueous ions and many complexes, based on a revised Helgeson-Kirkham-Flowers equation of state (HKF EoS), is now available in a SUPCRT92 database and its extensions (Shock and others, 1997, and references therein). This dataset, together with subroutines for HKF EoS calculations, is built into the GEM Selektor codes and used in all examples in the present study. In the codes, the ion association model of aqueous electrolyte (with chloride complexation) is supported by calculations of activity coefficients using the extended Debye-Hückel equation (Nordstrom and Muñoz, 1994, p.205) with individual Kielland's ion-size parameters for charged species and a common third parameter set to 0.064 as for NaCl background electrolyte. This equation produces the activity coefficients thought to be satisfactory up to unimolal effective ionic strength.

2.2. The Single-Site Triple Layer Model (TLM) of Surface Complexation

The single-site $2pK_A$ electrostatic TLM, suggested first by Yates and others (1974) and Davis and others (1978), has been further elaborated by Hayes and others (1991) and Sahai and Sverjensky (1997a,b). This mechanistic macroscopic SCM is based on the assumption that the oxide surface contains only one type of non-reacted site - *neutral amphoteric* ≡OH *functional group* - reacting with the bulk aqueous electrolyte by protonation, deprotonation, or ion binding into outer-sphere or inner-sphere surface complexes. The standard partial molal properties of surface complexes can be calculated via the respective adsorption reactions if such properties of a neutral ≡OH group are known. Knowledge of stoichiometry and G^o value of $\equiv OH^o$ functional group permits conversion of K^{int} into thermodynamic constants K_{A1}, $K_{A2,}$ $K_{Na,}$ $K_{Cl,}$ and K_M and into consistent G^o of surface complexes, to be used in GEM models of sorption.

2.3. Stoichiometry and Stability of the "Non-Reacted" >OH° Group

The neutral ≡OH surface group is usually considered to occupy "non-reacted" amphoteric sites because dry oxide surfaces fully hydr(oxyl)ate even in air at very low pressures of water vapour (Parks, 1990). If this is so, the elemental stoichiometry of the $\equiv OH^o$ species should be somehow related to water, with the ambiguity that elements inherent to the sorbent may or may not be included (for instance, $[TiO_{1.5}]OH^o$ versus OH^o). To resolve this ambiguity is a cornerstone decision in view of the future development of a unified thermodynamic database for surface species on mineral-water interfaces.

From the definition of the standard states (sec. 1.2.3), it follows that the inclusion of the sorbent stoichiometry would make partial molal properties of surface species dependent on composition and the specific surface area of the sorbent. Hence, thermodynamic data will be comparable for surface species existing on a single mineral only. With solid-solution sorbents or complex minerals such as clays, the situation would get even more complex because it is not always possible to fix stoichiometry of the mineral to be included in that of surface complexes, especially if different site types are involved. In the cases of large specific surface areas (for instance, 600 $m^2 \cdot g^{-1}$ for ferrihydrite HFO, Dzombak and Morel, 1990), the total mole fraction of surface species relative to the whole sorption phase may reach >0.2 (0.5 at standard state), and the stability of the sorbent and surface species will be seriously affected because the amount of sorbent $X_{\alpha,v}$ will strongly fluctuate with surface coverage. In LMA codes, the sorbent as such is not considered; the $\equiv OH^o$ master species is used to set up a balance constraint on total number of surface sites and define LMA expressions for surface complexes. So, the problem is not so relevant for LMA as it is for the GEM modeling approach.

For the above reasons, the choice *not to include stoichiometry of the sorbent into elemental stoichiometry of surface species* seems to be by far preferable. This choice would make standard thermodynamic properties comparable between different surfaces and minerals and also with that of aqueous sorbates, solids, and gases. To differentiate the surface species with the sorbent stoichiometry not included, a '>' symbol is used below instead of '≡'. Only monodentate surface species will be considered, if not otherwise stated. It is logical to begin with the "surface solvent" – the neutral amphoteric functional group $>OH^o$ that (hypothetically) occupies the whole sorbent surface at reference density Γ_o at the reference state (and at "infinite dilution" of surface complexes).

Although the value of $G^o(>OH^o)$ is unknown, it can be easily found by repeating GEM calculations of equilibrium with only one surface specices $>OH^o$ in the system "water – insoluble oxide (such as rutile) – air" at ambient conditions and negligible ionic strength near pH_{PPZC} (pristine point of zero charge). At such conditions, the $>OH^o$ species must exist close to its reference state, occupying all the oxide surface at reference density Γ_o; theoretical total number of moles of $>OH^o$ groups will be $\chi_n = A_{\alpha,v}X_{\alpha,v}M_{\alpha,v}\Gamma_o$. Criterion of adjustment is typical for an *inverse modeling problem*:

$$\text{minimize } \delta = (x_{jn} - \chi_n)^2 \qquad \text{by varying } G^o(>OH^o) \tag{37}$$

where x_{jn} stands for the calculated "equilibrium" number of moles of the $>OH^o$ surface species, with an initial guess G^o value taken as that for the aqueous OH^- ion (-157.3 $kJ \cdot mol^{-1}$ at 25°C). This calculation at $\Gamma_o = 20$ $\mu mol \cdot m^{-2}$ and different values of $A_{\alpha,v}$ and $X_{\alpha,v}$ results in $G^o(>OH^o) = -129.58 \pm 0.1$ $kJ \cdot mol^{-1}$, insensitive of pH, for any surface.

Such a numerical exercise can be performed for any conditional total density $\Gamma_C \neq \Gamma_o$, comprising a nice test for the validity of (eq 21). For instance, at $\Gamma_C = 1$ nm^{-2}, a value $G^C(>OH^o) = -123.31 \pm 0.1$ $kJ \cdot mol^{-1}$ has been obtained. The difference between G^o and G^C is 6.27 $kJ \cdot mol^{-1}$, or 1.098 pK units, while equation (21) predicts 1.081 pK units.

Once $G^o(>OH^o)$ is determined, the stability constants of surface complexation reactions can be converted into partial molal Gibbs energy G^o values of surface complexes, and vice versa. This conversion was done earlier for the DLM species of Zn on HFO (Kulik, 1995) and for the clay mineral surface species (Aja and Kulik, ms, 1997). However, further attempts to apply GEM modeling to redox-dependent sorption on the non-stoichiometric Mn oxides (Kulik and Kersten, 1998) revealed that the x_{jn} values, calculated using the OH^o elemental stoichiometry, strongly depend on the redox potential of the system. This stoichiometry is inadequate for the amphoteric surface functional group because it makes thermodynamic properties based on $G^o(>OH^o)$ effectively restricted to ambient conditions at atmospheric fugacity of oxygen gas ($fO_2 = 0.2$ bar). Therefore, a more adequate elemental stoichiometry of the neutral amphoteric surface group must be found.

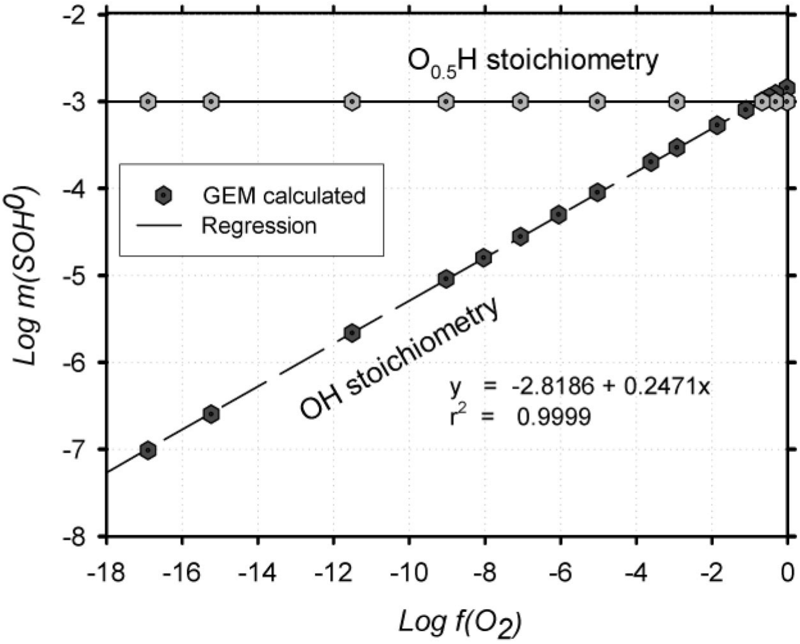

Fig. 1. Concentration dependence of the neutral >OH species on redox conditions (fO_2) in the system rutile- H_2O - air for the two possible stoichiometries: OH and $O_{0.5}H$.

To explore this problem, a hypothetical system with 0.01 m TiO_2 (sorbent) + 1 kg of water + 0.001 m NaCl + 1 g of air, with only one surface species $>OH^o$, was constructed in order to assess the dependence of calculated molality of surface $>OH^o$ group on fO_2. At $\Gamma_o = 20\ \mu mol \cdot m^{-2}$ and $A = 62.6\ m^2 \cdot g^{-1}$ (arbitrarily chosen for rutile), the theoretical amount of the $>OH^o$ groups is 0.001 mol. A series of equilibrium states has been computed with the GEM algorithm by adding/subtracting H_2 to/from the bulk composition of the system. 0.001 mol of the $>OH^o$ species was obtained at $fO_2 \approx 0.2$ bar, decreasing with fO_2 as $\log m(>OH^o) = -2.8186 + 0.2471 \cdot \log (fO_2)$ (fig. 1). A reason for such odd behavior might be that in OH^0 elemental stoichiometry of the $>OH^o$ group, the formal valence number of oxygen is −1, while in water and hydroxyl ion, this number is −2. A correct stoichiometry must yield G^o values insensitive to fO_2 at least within the stability field of water H_2O. Hence, next assumption was to try an $O_{0.5}H^o$ formula by a reaction

$$0.5H_2O_{aq} = >O_{0.5}H^o \qquad K_n \tag{38}$$

This reaction can be considered as a bidentate coordination of an H_2O molecule to a lattice metal and a lattice oxygen, with two hydrogen atoms shared between sites, yielding two neutral functional groups (of which only one is reactive). The model system was rebuilt for the new $O_{0.5}H^o$ stoichiometry, and the adjustment procedure (eq 37) re-run, resulting in $G^o(>O_{0.5}H^o) = -128.548\ kJ \cdot mol^{-1}$, *now insensitive* to fO_2 (see fig. 1), pH, amount and specific surface area of the sorbent.

From this value of G^o_{jn}, only 1 $kJ \cdot mol^{-1}$ different from that for the OH^0 stoichiometry at $fO_2 = 0.2$ bar, it follows that $\Delta G^o_n = -9.957\ kJ \cdot mol^{-1}$ and $\log K_n = 1.74436$. The value of $K_n = 55.5084$ is the same as the ratio $1000/M_w$ used for conversion from the molal to the mole fraction scales (eqs 14 and 33A), that is, $K_n = 1$

in rational (mole fraction) scale. The $>O_{0.5}H^o$ species can thus be regarded analogous to the water-solvent adsorbed at Γ_o density *on any* solid (hydr)oxide surface. Hence, the neutral amphoteric surface group macroscopically plays the role of an "aqueous surface solvent," rather than that of the surface-bound hydroxyl.

In view of this reasoning, the parameters of reaction (38) can be considered as *precise conventional values.* Furthermore, the reaction

$$>O_{0.5}H_2^+ = >O_{0.5}H^o + H^+_{aq} \qquad K_{A1} \tag{39}$$

can be regarded as detachment of a "surface hydronium ion" $>O_{0.5}H_2^+$, analogous to the reaction $(HOH)H^+ = HOH + H^+_{aq}$ in the bulk aqueous phase with conventional $K = 1$. In turn, a reaction

$$>O_{0.5}H^o = >O^-_{0.5} + H^+_{aq} \qquad K_{A2} \tag{40}$$

can be considered as dissociation of a surface-bound water $>O_{0.5}H^o$ into a "surface hydroxyl ion" $>O^-_{0.5}$ and an aqueous proton, again analogous to the dissociation of the bulk aqueous solvent, $HOH = OH^- + H^+$ (K_w).

This reasoning has deep consequences for determining other partial molal properties of surface species that define temperature behavior of pK_A and pH_{PZC}, addressed in detail elsewhere (Kulik, 2000). It permits us to define *the neutral amphoteric group as originating from a water molecule H_2O, bidentately coordinated to the oxide surface at reference density* according to reaction 38, with $\log K_n$ set to 1.74436 (in molal scale) at all temperatures and pressures.

Therefore, as follows from (eq 38) and in full accordance with (eq 33A), the equilibrium activity of the $>O_{0.5}H^o$ species

$$\ln a_n = \ln 55.5084 + 0.5 \cdot \ln a_w$$

must be independent of concentrations of other surface species, quantity and surface area of the sorbent, and nature of the surface. This conclusion is in apparent contradiction with a great variety of coordination environments, site geometries, densities and charges, that comprise the site heterogeneity found on oxide and silicate surfaces (Hiemstra and others, 1991; Charlet, 1994; Koretsky and others, 1998). However, one should keep in mind that the $>O_{0.5}H^o$ species considered here is essentially a thermodynamic entity, only needed to connect standard-state partial molal properties of surface complexes to that of chemical elements, aqueous ions, minerals, and gases.

The properties and stoichiometry of $>O_{0.5}H^o$, as such, imply no features of a particular surface geometry, arrangement and charge of the broken bonds, et cetera. Description of the hydroxylation of real surfaces may require stoichiometries and standard-state properties of adsorbed water molecules and hydroxyls different from that of the $>O_{0.5}H^o$ group. On many surfaces at the state of interest, the $>O_{0.5}H^o$ species may be unstable relative to surface complexes and will disappear because of surface (de)protonation, anion adsorption, cation surface complexation, binding of organic molecules, an so on. All such (metastable) equilibria should then be depicted with stoichiometry and thermodynamic properties of the "product surface species" defined via reaction chains, as well as with the maximum densities (or total site densities in case of competition). The usage of independent micro-spectroscopic observations, as well as molecular dynamics modeling to define stoichiometry and energetics of surface species in their coordination environments, seems to be an essential pre-requisite in setting up thermodynamic sorption models.

TABLE 5

TLM parameters for the LMA-calculated titrations of SiO_2,am in NaCl electrolyte

Parameter	**Value**	**Reference**
Total maximum site density	$4.6\ nm^{-2}$	SS97
Solid concentration	$30\ g \cdot L^{-1}$	B57
Solid specific surface area	$180\ m^2 \cdot g^{-1}$	B57
C1 capacitance density	$1.3\ F \cdot m^{-2}$	Fit
C2 capacitance density	$0.2\ F \cdot m^{-2}$	Fixed
log K_{A2} (reaction 40)	-7.7	SS97
log K_{Na} (reaction 42)	-6.9	SS97
Ionic strength (NaCl)	0.01; 0.1 M	B57

References: B57—Bolt, 1957
SS97—Sahai and Sverjensky, 1997a

PART 3. NUMERICAL EXAMPLES (AMBIENT CONDITIONS)

3.1. Amorphous SiO_2 in NaCl Electrolyte (TLM)

A simple application of the TLM is that for surface acidity of amorphous silica in a NaCl electrolyte. It is believed that silanol surface sites on silica cannot significantly protonate or attach electrolyte anions (Sposito, 1984). Hence, stability constants of reactions (39) and

$$>O_{0.5}H_2^+Cl^- = >O_{0.5}H^o + H^+_{aq} + Cl^-_{aq} \qquad (K_{Cl}) \qquad (41)$$

must be made weak, or both protonated species ($>O_{0.5}H_2^+$ and $>O_{0.5}H^+_{aq}Cl^-$) can be simply dropped; only reactions (40) and (42) are important:

$$>O_{0.5}H^o + Na^+_{aq} = >O^-_{0.5}Na^+ + H^+_{aq} \qquad (K_{Na}) \qquad (42)$$

The latest attempt at consistently fitting TLM parameters to the SiO_2,am potentiometric titration data of Bolt (1957) with an LMA code was made by Sahai and Sverjensky (1997a) for the parameters given in table 5. It was possible to reproduce their LMA model using FITEQL3.2 code (Kulik and Peretyashko, 1998); somewhat better fits were obtained after setting $C_1 = 1.3\ F \cdot m^{-2}$ (solid lines on fig. 2). Next, a GEM TLM has been set up for the same system Si - Na - Cl - H - O - charge (at T = 25°C, P = 1 bar) and computed using the GEM-Selektor code. Partial molal properties of aqueous species and gases were taken from the SUPCRT data set (Shock and others, 1997). Standard Gibbs energy of formation of amorphous silica was calculated from log K = −2.7 (Langmuir, 1997) of the reaction SiO_2,am = SiO_2,aq. G^o_j values for surface species were found using $G^o(>O_{0.5}H^o) = -128.55$ kJ $mole^{-1}$ and reactions (40) and (42) from pK^{int} values of the LMA model, converted to the reference density ($\Gamma_o = 12.05\ nm^{-2}$) using equation (21). The resulting thermodynamic data are listed in table 6. A maximum density constraint $\Gamma_{max} = 4.6\ nm^{-2}$ was set to apply the non-competitive SAT equation (29) for the $>O^-_{0.5}Na^+$ species. Titration points were generated by adding appropriate quantities of HCl or NaOH to bulk composition of

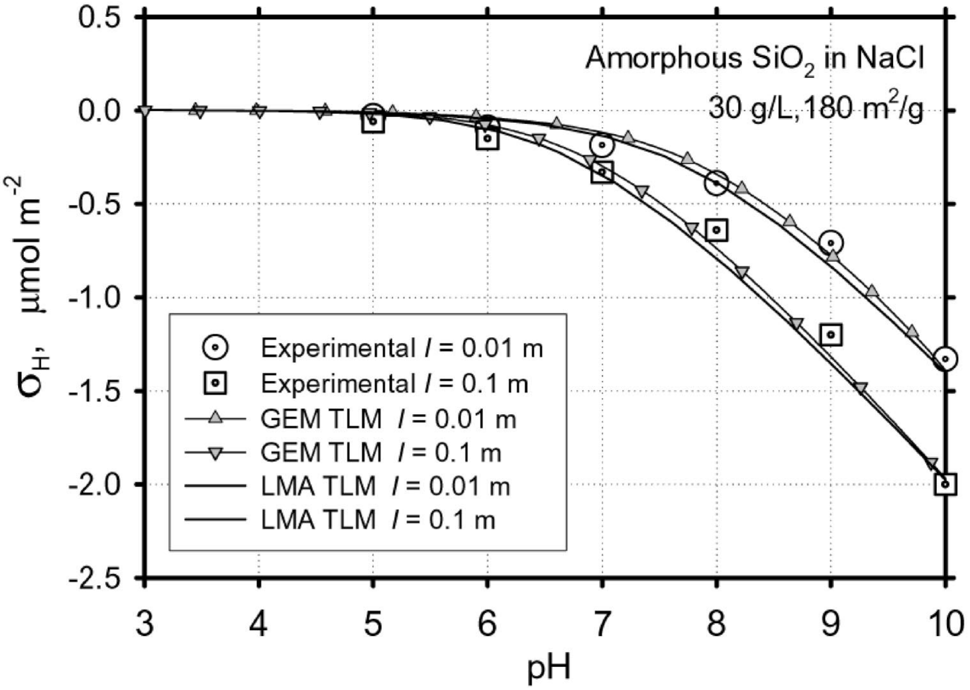

Fig. 2. Comparison of GEM and LMA fits for TLM of surface acidity of amorphous silica SiO_2 in NaCl electrolyte. Experimental data by Bolt (1957); see tables 5 and 6 for parameters.

the system composed of 30 g SiO_2, 985 g H_2O, and 0.01 or 0.1 moles NaCl. The surface proton charge was calculated as

$$\sigma_H = -(x(>O_{0.5}^-) + x(>O_{0.5}^-Na^+))/(x_{v,SiO_2}M_{v,SiO_2}A_{v,SiO_2})$$

The GEM runs resulted in a good fit with both experimental data and the LMA-calculated points (see fig. 2). Less than 2 percent of the surface proton charge was due to $>O_{0.5}^-$ species even at high pH. The SAT was always zero for the $>O^-Na^+$ complex, that is, the deprotonation of the silica surface in this system occurs in the "geometrically ideal region" and is not sensitive to $\Gamma_{max} \geq 4.6$ nm^{-2} (but sensitive to

TABLE 6

Thermodynamic data for surface species in GEM TLM of SiO_2,am in NaCl electrolyte

Species	**Reaction**	**log K**	**Stoichiometry**	**G^o_{298}, kJ·mol^{-1}**
$>O_{0.5}H^o$	38	1.74436	$O_{0.5}H$	-128.55
$>O_{0.5}^-$	40	-8.1	$O_{0.5}$-	-82.31
$>O_{0.5}^-Na^+$	42	-7.4	$O_{0.5}Na$	-348.19
SiO_2,am	^{A}	-2.7	SiO_2	-848.77

^{A} reaction SiO_2,am = SiO_2^o,aq

the TLM electrostatic correction factors and to C_1 parameter). Slight differences between the LMA and GEM-calculated curves can be explained by different implementations of the aqueous electrolyte model, namely inclusion of NaCl° complex and ionic silica aqueous species into the GEM calculations. The sum of all three surface species for all points was calculated to be close to that prescribed by $\Gamma_{max} = 4.6$ nm^{-2} assumed for silica surface. The SAT values for $>O_{0.5}H^o$ group (eq 36) increased with pH starting from $\ln \Xi_n = \ln (12.05/4.6) = 0.96$. The non-reacted OH group deviated from its reference state concentration even at pH = 3 by $\Xi_n = 2.6$ because of the $\Gamma_{max} < \Gamma_o$ condition. The presence or absence of the neutral $>O_{0.5}H^o$ species in the model did not influence the calculated proton surface charge curves at all.

3.2. The Amphoteric Rutile Surface

The next level of complexity is a single-site 2pK_A GEM TLM of an amphoteric surface capable of significant protonation under acidic conditions. Rutile (TiO_2) surface is suitable because of the numerous experimental studies in various electrolytes up to hydrothermal conditions (Machesky and others, 1998, and references therein). Rutile is practically insoluble and its surface does not exhibit significant effects of site heterogeneity. Reported maximum site densities for TiO_2 phases are around 12.5 nm^{-2} (Sahai and Sverjensky, 1997a), close to $\Gamma_o = 12.05$ nm^{-2} (the conventional value suggested in this contribution). In this context, rutile can be considered a "reference oxide surface" for thermodynamic adsorption modeling.

However, even for the relatively simple TiO_2 surface, the choice of TLM parameters in LMA sorption models remains ambiguous (Hayes and others, 1991). When the FITEQL code is used, it rarely converges if more than one TLM parameter is allowed to vary (Lützenkirchen, 1998). Ambiguities in defining TLM parameters have been sometimes considered as a justification of simplified models, such as the DLM (Dzombak and Morel, 1990) or the CCM (Schindler and Stumm, 1987). Can the new GEM approach be helpful in elucidating the thermodynamic background of the TLM? Are different combinations of TLM parameters really equivalent, or are some of them thermodynamically preferable? Answering such questions will be attempted below, using as an example GEM calculation of surface acidity of rutile at ambient conditions.

The TLM for the system TiO_2-H_2O-NaCl includes all five surface species described by reactions (39) to (42), allocated to the surface of the TiO_2 sorbent, plus the aqueous electrolyte phase. Summation of equations (39) and (40) results in a reaction

$$>O_{0.5}H_2^+ = >O_{0.5}^- + 2H^+_{aq}; \qquad \log K_{A12} = \log K_{A1} + \log K_{A2} = -2\ pH_{PPZC} \qquad (43)$$

which does not contain the neutral species $>O_{0.5}H^o$. This reaction also represents one important constraint on surface complexation models, related to the value of pH_{PPZC} (pH of pristine point of zero charge). For rutile, pH_{PZC} values of 5.4 to 6.4 have been reported at ambient conditions, as summarized by Sahai and Sverjensky (1997a). Subtraction of reaction (40) from (39) results in another important parameter ΔpK_A:

$$>O_{0.5}H_2^+ + >O_{0.5}^- = 2 > O_{0.5}H^o; \qquad \Delta pK_A = \log K_{A1} - \log K_{A2} \qquad (44)$$

Several authors (Hayes and others, 1991; Goldberg, 1991; Christl and Kretzschmar, 1999) found that this parameter can be made highly variable in the LMA fitting of titration data, because it is possible to obtain a good fit by adjusting ΔpK_A togther with the site density parameter Γ_C. Reaction (44) includes two "non-reacted" groups $>O_{0.5}H^o$, hence the transformation of ΔpK_A from one total site density Γ_{C1} to another Γ_{C2} (see sec. 1.3, eq 20) occurs as

$$\Delta pK_A^{(C2)} = \Delta pK_A^{(C1)} - 2 \log \frac{\Gamma_{C1}}{\Gamma_{C2}} \qquad (45)$$

TABLE 7

Thermodynamic data for the GEM TLM of rutile in NaCl electrolyte at 25°C, 1 bar (consistent with $C_1 = 1.7\ F \cdot m^{-2}$)

Species	**Reaction**	**logK**	**Stoichiometry**	**G^o_{298}, kJ·mol^{-1}**
$>O_{0.5}H^o$	38	1.74436	$O_{0.5}H$	-128.55
$>O_{0.5}H_2^+$	39	-2.2	$O_{0.5}H_2^+$	-150.24
$>O_{0.5}^-$	40	-8.6	$O_{0.5}$-	-82.88
$>O_{0.5}H_2^+Cl^-$	41	-3.9 ^{A}	$O_{0.5}H_2Cl$	-266.85
$>O_{0.5}^-Na^+$	42	-6.7 ^{B}	$O_{0.5}Na$	-350.47
Rutile			TiO_2	-888.79^C

^{A} Calculated from log K($O_{0.5}^-Na^+$) and $pH_{PZC} = 5.4$ assuming symmetric electrolyte adsorption.
^{B} Calculated from GEM-fitted value of $G^o_{298}(O_{0.5}^-Na^+)$.
^{C} Holland and Powell, 1990, Journal of Metamorphic Geology v. 8, p. 89–124. Parameters: 30 g · (kg $H_2O)^{-1}$ of rutile ($A = 17\ m^2 \cdot g^{-1}$) in 0.03 m NaCl electrolyte. logK for $>O_{0.5}H_2{}^+$ and $>O_{0.5}^-$ species were calculated from $pH_{PZC} = 5.4$ (Machesky and others, 1998) and $\Delta pK_A = 6.4$ (Sahai and Sverjensky, 1997a) and then fixed while fitting G^o_{298} of the outer-sphere Na surface complex. $\Gamma_{max} = 12.5$ sites · nm^{-2} was set for $>O_{0.5}H^o$ and $>O_{0.5}^-Na^+$ species, and $\Gamma_{max} = 0.85$ sites · nm^{-2} for the $>O_{0.5}H_2^+Cl^-$ surface complex.

An immediate consequence is that at the reference density Γ_o, there can only be a unique value of ΔpK_A that yields (at a given pH_{PPZC}) unique values of the standard-state constants pK_{A1} and pK_{A2}. Together with the pH_{PPZC} constraint (eq 44), this fact requires that a *unique set of standard thermodynamic values must exist for each oxide surface type.* All other combinations (at different ΔpK_A) must *involve at least one more parameter,* for instance, a function of maximum site density and/or the EDL model. The question is how to find this optimal set of standard thermodynamic properties from the experimental data.

3.3. Rutile in NaCl Electrolyte (Comparison of TLM, NEM and DLM Fits)

The objective of this example was to investigate sensitivity of GEM fits to variations of TLM parameters and to find the "optimal" input data set for an example of rutile in 0.03 M NaCl electrolyte at 25°C (titration data by Machesky and others, 1998). This example is just one curve of the full set of GEM TLM fits to 250°C described elsewhere (Kulik, 2000). Since $>O_{0.5}^-$ and $>O_{0.5}H_2^+$ surface species comprise in TLM only a small percentage of the total surface proton charge, pK_{A1} and pK_{A2} values were fixed using pH_{PPZC} and ΔpK_A values (table 7). To obtain better fits at pH < 5, the $>O_{0.5}H_2^+Cl^-$ outer-sphere species had to be constrained by an individual SAT with $\Gamma_{max} = 0.85$ nm^{-2}. Total proton surface charge density on rutile σ_H was calculated from surface species mole quantites x_j as follows:

$$\sigma_H = [x(>O_{0.5}H_2^+) - x(>O_{0.5}^-) + x(>O_{0.5}H_2^+Cl^-) - x(>O_{0.5}^-Na^+)]/(X_{v,r}M_{v,r}A_{v,r})$$

(in μmol · m^{-2}), where $X_{v,r}$, $M_{v,r}$, $A_{v,r}$ are number of moles, gram-formula mass and specific surface area of rutile. Goodness of GEM fits was estimated graphically, no formal procedure for minimizing deviations between calculated and experimental data was applied.

Calculations showed that G^o values for $>O_{0.5}H_2^+Cl^-$ and $>O_{0.5}^-Na^+$ species cannot be adjusted independently of the Stern layer TLM capacitance parameter C_1. Smaller C_1 values result in flatter proton surface charge curves and require stronger stabilities of both surface species and vice versa. However, it is possible to find a C_1 value producing the same curvature as the measured points, and then adjust G^o_{Na} and log K_{Na}. Results of this exercise are presented as solid lines in figure 3. The fit at $C_1 = 1.7\ F \cdot m^{-2}$ is quite good, a small deviation at pH values between 6 and 7 can be removed only at the cost of introducing another (minor) surface site type. The surface speciation lines (fig. 3B) display linear parts near pH_{PZC}, where the EDL correction is still small, then, they bend at lower and higher pH. Variation of C_1 while other parameters fixed to the values in table 7 produces a family of σ_H curves (dotted lines on fig. 3). All fits are in the "geometrically ideal TLM behavior" region (except a small area at low pH). Hence, only one value of $C_1 \approx 1.7 \pm 0.1\ F \cdot m^{-2}$ is consistent with the standard state data in table 7.

Even the TLM fits with an *ad hoc* value of $C_1 = 3.7\ F \cdot m^{-2}$, for which the adsorption constants from table 7 are far too strong, can be made satisfactory upon the introduction of a competitive SAT for all species at small enough $\Gamma_{t,max} = 1.2\ nm^{-2}$, as shown on figure 4. However, this procedure throws the TLM into the "geometrically non-ideal" region, with quite large SAT values at both sides of pH_{PZC} (fig. 4C) creating typical Langmuirian bends (fig. 4A and B). The introduction of non-ideality greatly improves the fit but results in obviously non-optimal, inconsistent combinations of TLM parameters. The value of Γ_{max} chosen for the fits (fig. 4) is physically meaningless. Since the SAT (function of Γ_{max}) in GEM approach works similar to the balance constraint $N_{t,s}$ on total amount of surface sites in the LMA approach, the plot (fig. 4) illustrates the possible consequences of inappropriate usage of the site density parameter for SCM fitting of potentiometric titration data.

The "ideal" GEM NEM fit (dashed line on fig. 5) uses all thermodynamic data from table 7, except that the EDL correction (Ψ in the Coulombic term) was always set to zero, and SAT were set to 1. The fact that NEM provides almost as good a fit between pH 4 to 7 as the "optimal" TLM (see fig. 3) suggests that *both SCMs behave asymptotically correct on approach to the reference state for surface species,* in full accordance with equations (9) and (10). This conclusion is further corroborated by the log-linear NEM surface speciation plots versus pH near pH_{PZC} (fig. 5B). Very large deviations of the ideal NEM from experimental points at $pH < 4$ and $pH > 7$ also demonstrate the power of TLM electrostatic corrections and Coulombic terms. Interestingly, the formally good (in a sense of SOS/DF criterion used in the FITEQL code) NEM fits can be obtained artificially, in exactly the same way as the fits for the "non-optimal" TLM - by introducing strong enough SAT correction at $\Gamma_{max} = 0.75\ nm^{-2}$ (solid lines on fig. 5). This procedure leads to SAT values up to 2000 and more (fig. 5C), which can be considered as a (related to non-ideality) maximum error estimate introduced into the intrinsic constants K^{int} by the LMA fitting of titration data with an inappropriate set of SCM parameters.

Dzombak and Morel (1990) suggested a Generalized Diffuse Double Layer model (DLM) for hydrous ferric oxide (HFO) that became very popular and widely applied to various experimental and environmental systems, so it was of interest to see how it might work in GEM implementation on our example of rutile titration data. DLM does not account for the electrolyte adsorption and, for obtaining the surface potential Ψ, uses only the Gouy-Chapman equation (see Morel and Hering, 1993), the latter depending on surface charge density, temperature, and ionic strength. The Na and Cl outer-sphere surface species were thus simply dropped. Model curves were calculated with the remaining species at $\Delta pK_A = 6.4$ and no SAT corrections, except for the $>O_{0.5}H^o$ group (dotted line on fig. 6A). Of course, this procedure resulted in a poor DLM fit due to neglected development of surface proton charge by the electrolyte adsorption. The DLM fit could be improved just by selecting a small enough $\Delta pK_A = 2.0$ (dashed line on fig. 6A), making K_{A1} and K_{A2}

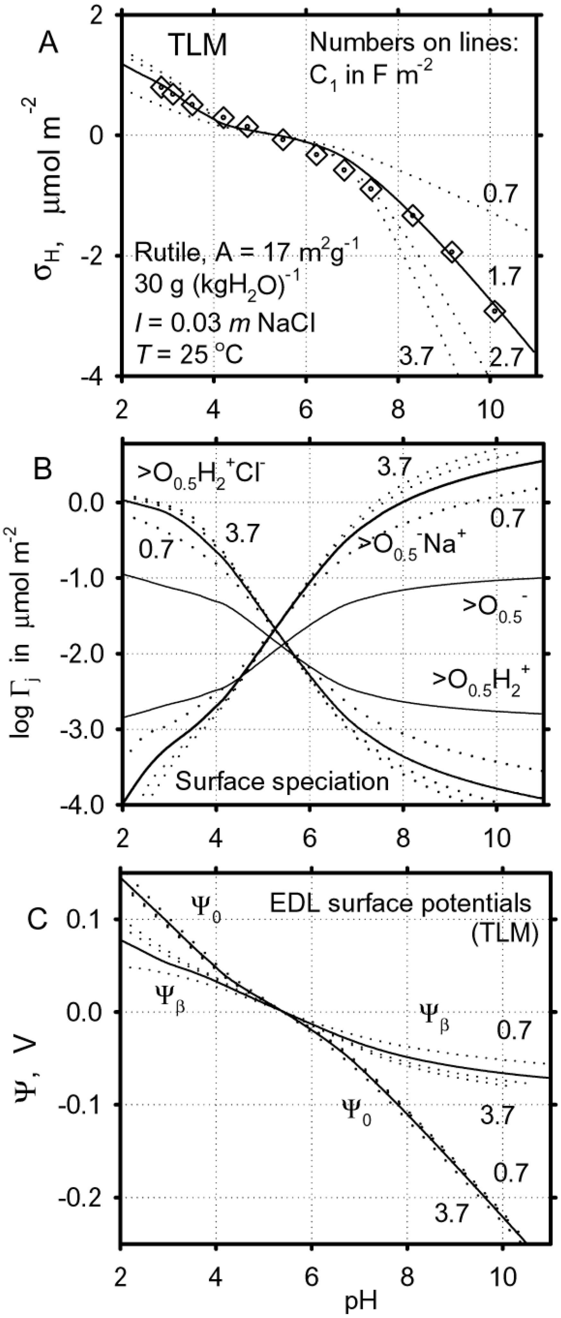

Fig. 3. GEM TLM fits of potentiometric titration data for rutile in 0.03 m NaCl electrolyte at 25°C (experimental data by Machesky and others, 1998). Solid lines: "optimal" fit at $C_1 = 1.7\ F \cdot m^{-2}$. Dotted lines: non-optimal fits at other values of C_1 (numbers on lines). The $>O_{0.5}H^+Cl^-$ species is corrected by a SAT at $\Gamma_{max} = 0.85\ nm^{-2}$. Other TLM parameters are given in table 7.

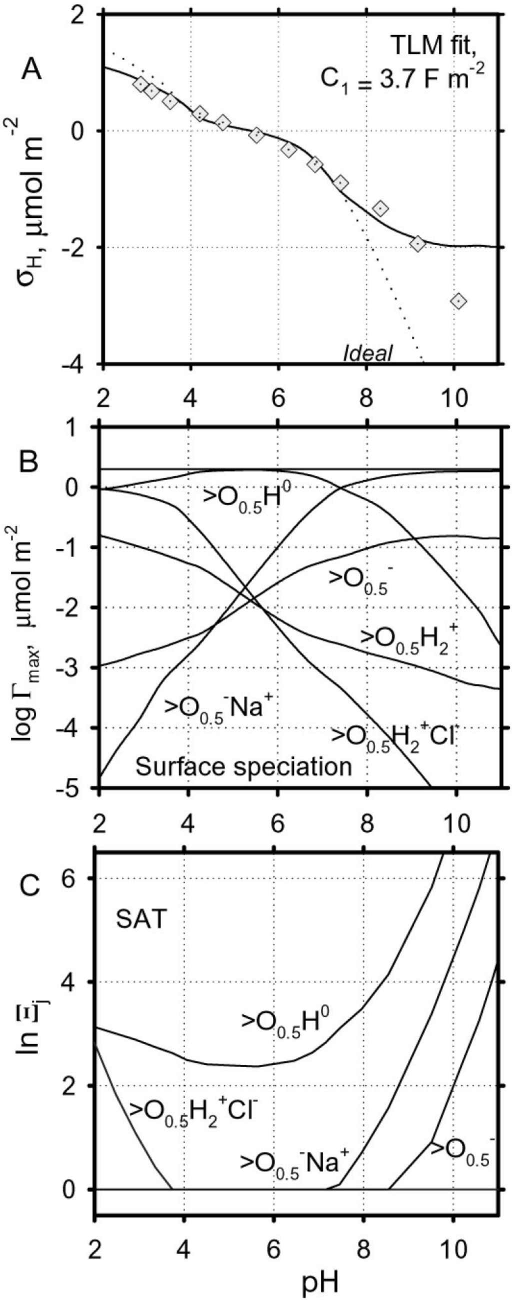

Fig. 4. A "non-ideal" GEM TLM fit for rutile in 0.03 m NaCl at a non-optimal $C_1 = 3.7$ F · m^{-2} with a non-competitive SAT constraint at $\Gamma_{max} = 0.6$ nm^{-2} for $>O_{0.5}H^+Cl^-$ species and competitive SAT corrections at $\Gamma_{max} = 1.2$ nm^{-2} for other surface species. Dotted line: "ideal" fit.

each 160 times stronger. However, the DLM electrostatic correction appears to be too weak for such a "stability distortion effect", resulting in a large deviation of the "ideal" DLM at pH < 3.5 and pH > 7.5.

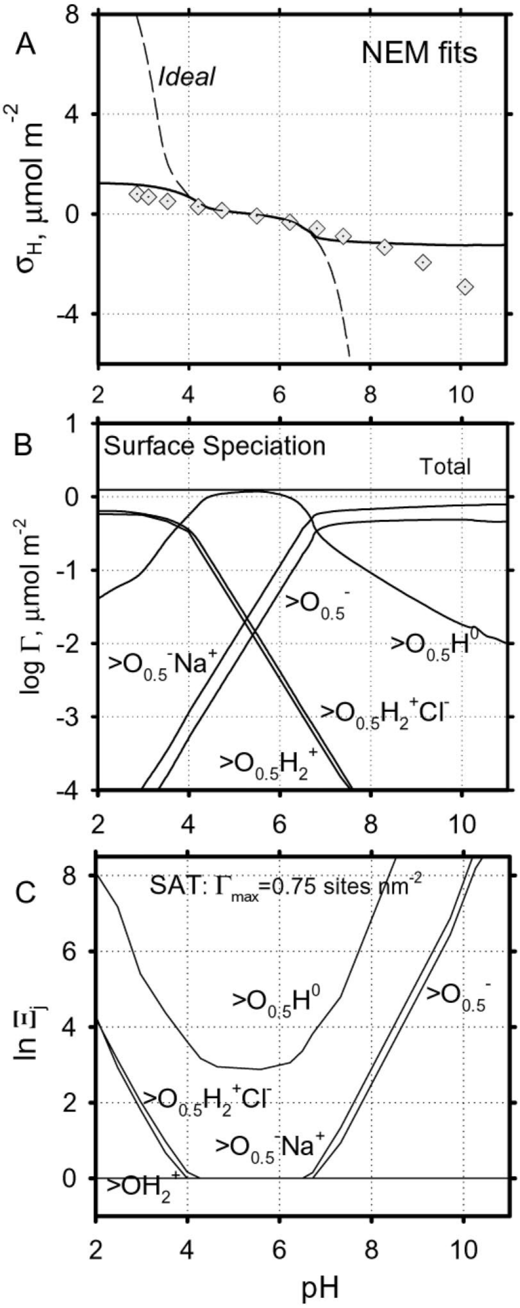

Fig. 5. GEM NEM fits for rutile in 0.03 m NaCl. Dashed line: an ideal fit with thermodynamic data from table 7. Solid lines: a strongly non-ideal fit with competitive SAT at $\Gamma_{max} = 0.75 \text{ nm}^{-2}$.

Thus, it appears that neglect of electrolyte adsorption, in principle, restricts the thermodynamic adequacy of DLM only to a certain concentration of background electrolyte. Yet, the DLM fits to titration data can be made formally good, again by

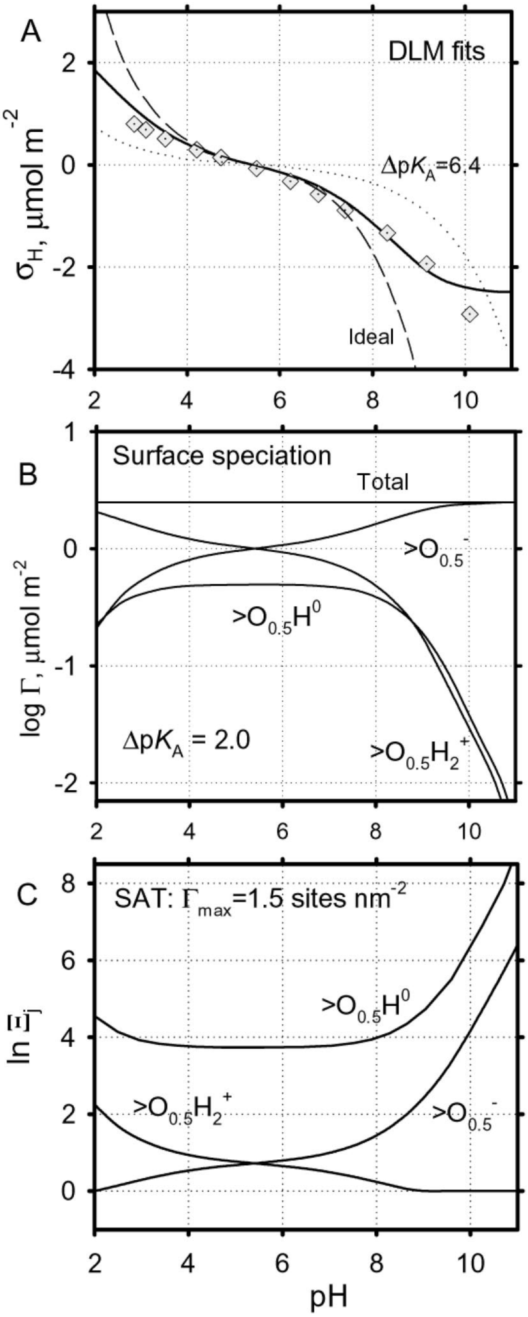

Fig. 6. GEM DLM fits for rutile in 0.03 m NaCl at different ΔpK_A values (6.4, dotted line; 2.0, dashed line). Solid lines: a "best" non-ideal fit with competitive SAT at Γ_{max}=1.5 nm^{-2} for all surface species.

biasing the model into the geometrically non-ideal region by introducing the competitive SAT constraints at $\Gamma_{t,max} = 1.5$ nm^{-2} (solid lines on fig. 6). As in the NEM case, this procedure resulted in quite a large increment of SAT into the intrinsic adsorption constants. The neutral $>O_{0.5}H^o$ species also had quite high SAT value even at pH_{PZC} ($\ln \Xi_n \geq 3.7$, fig. 6C), and this SAT is quite different from that of $>O_{0.5}H_2^+$ and $>O_{0.5}^-$ species in the whole pH interval. The following questions arise: what is actually included into the values of intrinsic NEM, TLM, and DLM adsorption constants routinely estimated in the LMA fitting of titration data? Do such systems exist where the SAT corrections and Γ_{max} parameters are really unavoidable in description of sorption on heterogeneous surfaces with the help of thermodynamic SCMs? Are Γ_{max} parameters just fudge factors, or can these values be deduced from independent micro-spectroscopic and crystallographic data? What Γ_{max} values should be taken if such data are not available?

3.4. Sorption of Cr^{III} on SiO_2,am

Fendorf and others (1994), and Fendorf and Sparks (1994) studied an uptake of dissolved Cr^{III} by $0.25\ g \cdot L^{-1}$ amorphous silica SiO_2,am at pH between 3.5 and 6.5 in 0.1 M $NaNO_3$ electrolyte at relatively high total chromium (10^{-4} M). Using EXAFS and HRTEM, these authors discovered the formation of surface clusters of a γ-CrOOH structure on silica surface at pH > 5.5; at lower pH, a monodentate surface complexation of Cr^{III} seems to form. Similar phenomena are known also for Cr^{III} sorption on MnO_x, Cr^{III} on FeOOH, and Cu sorption on Al oxides (McBride, 1982; Karthikeyan and others, 1997). The shapes of pH steps of Cr^{III} adsorption measured by Fendorf and others (1994) at 3.5 < pH < 5.5 also suggest binding of chromium into "strong" and "weak" surface complexes. Sorption of Cr^{III} on SiO_2,am can be modeled in the whole experimental pH interval using a simple two-site GEM NEM, with allowed (surface) precipitation of a CrOOH,s phase. More details and comparison to the LMA SCM are given elsewhere (Kulik and Peretyashko, in preparation).

The model system SiO_2-H_2O-$NaNO_3$-$Cr(OH)_3$ was constructed in Ar-Cr-H-N-Na-O-Si-charge elemental stoichiometry basis. Aqueous electrolyte species, water, gaseous (Ar, H_2, O_2), CrOOH solid, and SiO_2,am sorption phases were included. Bulk composition of the system was built from 1 kg H_2O, 1 g of air with 0.03 g H_2 to maintain reducing conditions, 0.25g SiO_2, 10^{-4} mol $Cr(OH)_3$, and 0.1 mol $NaNO_3$. Model titrations were performed by additions of HNO_3 or NaOH to the bulk system composition. Thermodynamic data at T = 25°C and P = 1 bar for all species except Cr^{III} surface complexes and solids was taken from the SUPCRT database. The $O_{0.5}Cr(OH)_2^o$ elemental stoichiometry was used to describe the "strong" and "weak" binding of Cr^{III} onto silica surface via the reactions:

$$>O_{0.5}H^o + Cr^{3+} + 2H_2O = >sO_{0.5}Cr(OH)_2^o + 3H^+$$

$$>O_{0.5}H^o + Cr^{3+} + 2H_2O = >wO_{0.5}Cr(OH)_2^o + 3H^+$$

The values of $G^o(>sO_{0.5}Cr(OH)_2^o)$, $G^o(>wO_{0.5}Cr(OH)_2^o)$, G^o(CrOOH,s), and the maximum density parameter for "strong" sites $\Gamma_{max,ss}$ (table 8) were fitted in GEM calculations. Titration at 3 < pH < 9 were performed as a sequence of inverse titration problems. $\Gamma_{max} = 9.133\ \mu mol \cdot m^{-2}$ ($5.5\ nm^{-2}$) was set for the $>O_{0.5}H^o$, as well as for the species competing on "weak" sites: $>O_{0.5}H_2^+$, $>O_{0.5}^-$, $>wO_{0.5}Cr(OH)_0^{2w}$. Removal of the $>O_{0.5}H_2^+$ and $>O_{0.5}^-$ species from the GEM NEM formulation did not significantly change any fits for Cr^{III} sorption. No competition was assumed for the "strong-site" $>sO_{0.5}Cr(OH)_2^o$ species, constrained by a SAT (eq 29) at $\Gamma_{max,ss} = 0.332\ \mu mol \cdot m^{-2}$. Calculation results were plotted on figure 7 in two variants: CrOOH,s phase included and excluded.

Figure 7A shows that the GEM NEM with two-site adsorption of Cr^{III} hydroxocomplex and precipitation of CrOOH,s provides a quite reasonable fit to experimental data. As seen on figure 7B, mainly the $>sO_{0.5}Cr(OH)_2^o$ species exists up to pH = 5. At pH ≈ 4.5, the "strong" sites get saturated, and the $>wO_{0.5}Cr(OH)_2^o$ species accumu-

TABLE 8

Thermodynamic data for the GEM NEM of Cr^{III} sorption on SiO_2,am at 25°C, 1 bar

Species	Γ_{max}, nm^{-2}	Reaction	log K	Stoichiometry	G^o_{298}, $kJ \cdot mol^{-1}$
$>O_{0.5}H^o$	5.5	38	1.74436	$O_{0.5}H$	-128.55^A
$>O_{0.5}^-$	5.5	40	-8.1	$O_{0.5}$-	-82.31^A
$>wO_{0.5}Cr(OH)_2^o$ (weak)	5.5	D	-12.1	$O_{0.5}Cr(OH)_2$	-740.12^B
$>sO_{0.5}Cr(OH)_2^o$ (strong)	0.2^C	D	-9.11	$O_{0.5}Cr(OH)_2$	-758.33^C
SiO_2,am (sorbent)			-2.7^A	SiO_2	-848.77
CrOOH,s phase		E	-10.0	CrOOH	-623.49^B

Parameters of the system: $0.25\ g \cdot L^{-1}$ SiO_2,am ($A = 221\ m^2 \cdot g^{-1}$) in 0.1 M $NaNO_3$, 10^{-4} M total Cr.
[A] See Table 6
[B] Adjustable parameters in GEM calculations at $pH > 5.0$
[C] Adjustable parameters in GEM calculations at $pH < 5.0$; non-competitive SAT
[D] Reaction $>O_{0.5}H^o + Cr^{+3} + 2H_2O = >O_{0.5}Cr(OH)_2^o + 3H^+$
[E] Reaction $Cr^{+3} + 2H_2O = CrOOH,s + 3H^+$

lates simultaneously to some extent up to $pH \approx 5.5$. At this point, the CrOOH,s phase becomes stable, and its precipitation fixes the $Cr(OH)_3$ activity in aqueous solution when the pH increases further. Consequently, the surface density of the $>wO_{0.5}Cr(OH)_2^o$ species remains constant (fig. 7B) without any SAT contribution (fig.7C). The SAT for $>sO_{0.5}Cr(OH)_2^o$ species strongly increases from $\ln \Xi \approx 0$ at $pH = 4$ up to $\ln \Xi \approx 5.8$ at $pH \approx 5.2$, then remains more or less constant ($\ln \Xi$ fluctuating around 6), again consistent with the fixation of the chemical potential of $Cr(OH)_3$ in aqueous solution due to precipitation of the solid Cr^{III} hydroxide phase. If the latter is excluded then the model significantly under-predicts the sorption of Cr^{III} at $5.5 < pH < 6.5$ (dashed lines on fig. 7A and B).

Thermodynamics cannot tell us whether Cr^{III} hydroxide is precipitated into separate particles or into surface clusters - a preferable mechanism according to Fendorf and Sparks (1994). However, it is unlikely that surface precipitation would significantly change the amount of reactive SiO_2 surface in this system. As seen in figure 7B, the maximum density of CrOOH,s, if it were to precipitate as a "surface monolayer" only, is less than $0.8\ nm^{-2}$, or 7 times less than $\Gamma_{t,max} = 5.5\ nm^{-2}$ assumed for the amorphous silica sample. Surface clusters, in reality, must be multi-layered, so they can cover at most 1 to 2 percent of the silica surface. From the GEM NEM speciation it follows that, as long as the surface precipitates are stable, the activity of $Cr(OH)_3$,aq is constrained by the solubility of CrOOH,s, and hence no changes in densities of Cr^{III} surface complexes are likely to occur (fig. 7B). Any further complication of GEM NEM is not warranted.

Note that this model is rather sensitive to variations in the values of $G^o(>wO_{0.5}Cr(OH)_2^o)$ and G^o(CrOOH,s), which are inter-related. For instance, a 1.0 $kJ \cdot mol^{-1}$ more negative value of the first parameter makes the weak monodentate Cr^{III} surface complex binding up to $0.4\ nm^{-2}$, at the same time it requires that the G^o(CrOOH,s) value becomes about 0.5 $kJ \cdot mol^{-1}$ more positive in order to maintain a good fit to the experimental adsorption data, which are rather scarce for more precise determination of these two thermodynamic constants.

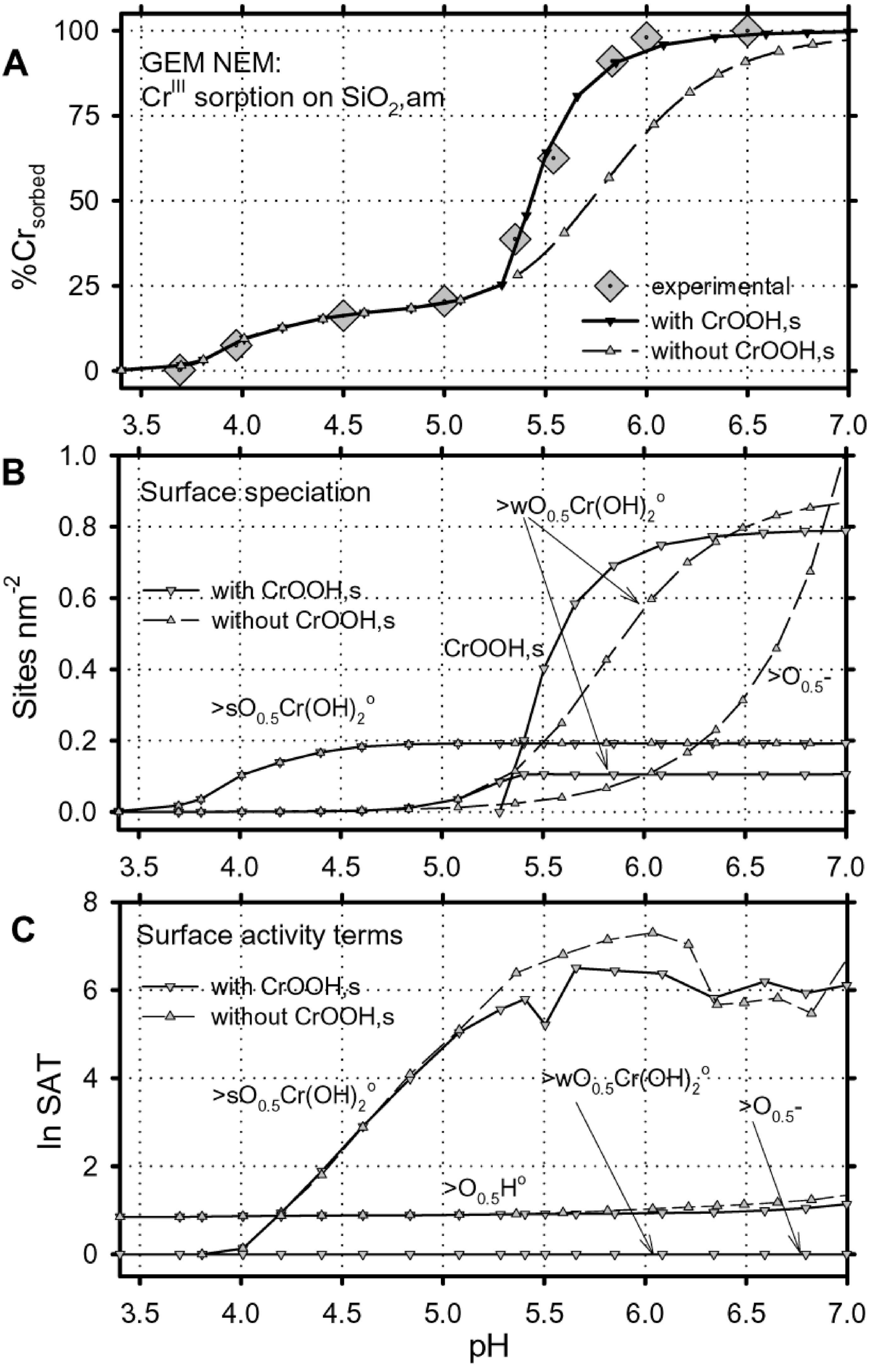

Fig. 7. A GEM NEM fit of heterogeneous sorption of Cr^{III} on SiO_2,am in $NaNO_3$ (see table 8 for thermodynamic data and system parameters; experimental data: Fendorf and others, 1994). (A) Total sorption of Cr^{III} (dashed line – solid CrOOH,s phase excluded); (B) calculated surface speciation (including "surface density" of CrOOH,s; the real CrOOH surface clusters are multi-layered and occupy less than 1–2 percent of the total SiO_2 surface); (C) Calculated surface activity terms; small irregularities of ln Ξ at pH > 5.5 result from stiff numerical behavior of equation (29) but do not affect calculated density of the $>O_{0.5}Cr(OH)_2^o$ species (see plot B).

PART 4. DISCUSSION

The following LMA expressions can be written using SAT for the surface deprotonation reactions given in equations (39), (40) and (43):

$$\equiv OH_2^+ = \equiv OH^o + H^{aq}_{+}, \qquad K_{A1} = \frac{m(\equiv OH^o)\cdot \Xi(\equiv OH^o)}{m(\equiv OH_2^+)\cdot \Xi(\equiv OH_2^+)}\cdot m(H^+_{aq})\cdot \gamma(H^+_{aq}) \tag{46}$$

$$OH^o = \equiv O^- + H^+_{aq}, \qquad K_{A2} = \frac{m(\equiv O^-)\cdot \Xi(\equiv O^-)}{m(\equiv OH^o)\cdot \Xi(\equiv OH^o)}\cdot m(H^+_{aq})\cdot \alpha(H^+_{aq}) \tag{47}$$

$$\equiv OH_2^+ = \equiv O^- + 2H^+_{aq}, \qquad K_{A12} = \frac{m(\equiv O^-)\cdot \Xi(\equiv O^-)}{m(\equiv OH_2^+)\cdot \Xi(\equiv OH_2^+)}\cdot m(H^+_{aq})^2\cdot \alpha(H^+_{aq})^2 \tag{48}$$

A common opinion is that the activity coefficients of surface species are unknown and cannot be directly measured but must probably cancel out in the LMA expressions (Davis and Kent, 1990; Dzombak and Morel, 1990). Theoretical reasoning and previous examples introduce the SAT indeed akin to the activity coefficients. They can, in fact, compensate each other in (eq 48) as long as the Γ_{max} is large enough to keep the system in the region of "geometrically ideal SCM behavior" (as the "optimal" TLM on figs. 2 and 3 or NEM in the vicinity of pH_{PZC}, fig. 5A). If the fitting is performed in the geometrically non-ideal region (for example, fig. 6), the SAT ratio in (eq 48) will be different from unity everywhere except, maybe, at the pH_{PZC} point. This ratio actually measures how the intrinsic equilibrium constant K^{int} deviates from the thermodynamic one K under the influence of the SAT $\Xi_j = f(\Gamma_{max})$ corrections.

Another SAT ratio applies to the reactions involving the ≡OH° species. Reasoning provided in sec.1.3 (eq 36), backed up by numerical examples (figs. 5 and 6), shows that the SAT ratio (Ξ_j/Ξ_{jn}) in reactions such as (eqs 46 and 47) can be unity only at the reference state, at the physically unattainable "infinitely low coverage" of surface complexes. In real systems, this ratio will deviate from 1 even in the "geometrically ideal SCM region" (all $\Xi_j = 1$); the smaller $\Gamma_{t,max}$ value imposed, the stronger the deviation. For instance, it follows from the GEM DLM fit (fig. 6C) that the SAT ratio (reaction 47) $\Xi(\equiv O^-)/\Xi(\equiv OH^o) < 0.13333$, or nearly -0.9 log units, in the example where $\Gamma_{t,max} = 1.5\ nm^{-2}$ was set.

The SAT ratios involved in (eqs 46 or 47) may also be considered as second-order effects related to conversion of K^{int} between different total site densities Γ_C and/or Γ_o (eq 21). This equation, as such, compares reference states of neutral surface functional groups ≡OH° between Γ_{C1} and Γ_{C2}. In real systems, the ≡OH° groups never exist at the reference state in the presence of surface complexes (see eq 36 for SAT Ξ_{jn}). The higher the total density of "reacted" groups (that is, surface complexes), the greater is the deviation, and the magnitude of the deviation is the higher the smaller the total site density chosen! More work to find equations for second-order corrections to (eq 21) is therefore necessary.

The reasoning provided above highlights a major weakness of $2pK_A$ SCMs: inclusion of the non-reacted functional group (≡OH° species for amphoteric surfaces) makes the LMA-fitted K^{int} values highly sensitive to the selected total Γ_C and maximum $\Gamma_{t,max}$ site density and ΔpK_A. The smaller these parameters, the stronger is the increment of $\Xi(\equiv OH^o)$ and SAT of surface complexes in the geometrically non-ideal region for the LMA expressions (like eqs 46 and 47). Conversely, large ΔpK_A and $\Gamma_{t,max}$ parameters, which provide the near-unity SAT ratios as in the GEM TLM (fig. 3), are thermodynamically justified and preferable. Smaller ΔpK_A and $\Gamma_{t,max}$ may only be introduced for description of site heterogeneity effects or multi-site adsorption, if their use is supported by the independently obtained microscopic, spectroscopic and kinetic information.

A strong feature of GEM SCMs is that the increments from standard thermodynamic properties, EDL Coulombic corrections, and Γ_{max} (SAT) constraints are considered separately (see eq 14). This procedure permits us to directly fit the standard partial molal G^o values for surface complexes of the chosen elemental stoichiometry in GEM batch calculations. Then, the thermodynamic constants of reactions like (39) to (42) can be calculated, and the deviations between modeled and measured titration curves can be analyzed. As seen from previous numerical examples, different GEM SCM fits of experimental pH steps or acid-base titration data are possible, but a *criterion of quality is obviously the minimum of constraints imposed in addition to the standard-state thermodynamic data.* Hence, the GEM model fits with the widest "geometrically ideal region" insensitive to Γ_{max} should be considered *optimal.* Application of this criteria can be viewed as a new strategy of TLM parameter set optimization.

Because TLM and NEM appear to have the same behavior near the reference state, it may be recommended to begin with the NEM, applied to the same set of surface species as in TLM and restricted to several titration points measured close to pH_{PZC} at low ionic strength (for example, at pH 4–7 on fig. 5A). This step permits the adjustment of G^o values of the $\equiv O^-$, $\equiv OH_2^+$ species, and adsorbed electrolyte ions in such a way that correct pH_{PZC} and the slope of σ_H curve are reproduced. Independent measurements of cation and anion adsorption near pH_{PZC} can be very helpful at this stage. Next, the TLM EDL correction is applied, and only the C_1 parameter is adjusted for the best fit of the measured points at a large enough value of $\Gamma_{t,max}$ (for example, $\Gamma_{t,max} = \Gamma_o$) and different concentrations of background electrolyte. The remaining deviations (if any) can be accounted for in a third stage by applying individual (or competitive) SAT constraints at lower $\Gamma_{t,max}$ values or by introducing other surface types and sites to account for the surface heterogeneity. Surface precipitation effects can be accounted for in GEM SCMs by introducing a separate solid phase for the sorbate (see fig. 7) or, in certain cases, by setting a *very large* $\Gamma_{max} >> \Gamma^o$ parameter for a neutral precipitate species, to allow multi-layer "adsorption" on a small-area surface type.

Banwart (1997) points out that the current understanding of the factors resulting in the non-ideal adsorption behavior is still poor. According to Schindler and Stumm (1987), one reason for this state of affairs can be attributed to Coulombic contribution to the total adsorption and solvation energy for charged sorbates and to their electrochemical potentials (eq 14). Electrostatic SCMs present different ways of relating this contribution to EDL properties and charging behavior of the surface; accordingly, different parameter values are obtained for the same set of titration data. Two other reasons can also be mentioned: (1) a heterogeneous surface with a distribution of adsorption intensities (expressed macroscopically by the Freundlich isotherm); (2) lateral interactions between adsorbed species, described, for instance, by the Frumkin-Fowler-Guggenheim (FFG) isotherm. Experimental titration data often represent a combination of several effects, and it is of essential importance to separate them in thermodynamic models using any available micro/spectroscopic or crystallographic information.

In this respect, the GEM SCM thermodynamic approach provides at least three new tools. It follows from equation (14) that it is possible to allocate surface species to different surface patches, or types, each occupying a certain fraction $\phi_{\alpha,t}$ of the total reactive surface area of the sorbent. The word "reactive" means that $\Sigma\phi_{\alpha,t}$ does not necessarily equal unity – some faces of crystalline mineral particles may be non-reactive, or some more reactive surface may become available on cracks during experiments, interlayer in frayed edges of clay particles, and so on.

Each surface type may have its own maximum accessible site density $\Gamma_{t,max}$, defined by crystallographic arrangement or structural defects and reflected through the competitive SAT Ξ_j, $j \in l_{\alpha,t}$. Certain sorbates may attach themselves to highly specific sites of low density $\Gamma_{t,j,max}$ in a non-competitive way, in which case, the non-competitive SAT corrections must be applied. Finally, concentrations of charged surface species are affected by electrostatic interactions, described via the Coulombic term with the surface potential $\Psi_{\alpha,t}$ defined according to the EDL model chosen for a given surface type, in turn, dependent on $\Gamma_{t,max}$ parameters. Microscopic/spectroscopic knowledge about the surface structure can and should be used for selection of the appropriate surface and site types and derivation of the proper SAT equations. A lot of work on reconsidering titration data sets in this manner still has to be done.

Naturally, the GEM SCM thermodynamic modeling described in this contribution still has some drawbacks, or, more precisely, shortcomings and limitations, which are mentioned below. Future studies will reveal which of these shortcomings are critical and need to be eliminated, and which are irrelevant or can be worked around.

Experimental sorption data are often expressed as distribution ratios, R_d, or distribution coefficients, K_d, traditionally used in contaminant migration modeling and performance assessment of waste repositories. Both coefficients are defined as the ratio of element concentration bound to the solid sorbent (in $mol \cdot kg^{-1}$) to element concentration in aqueous phase (in $mol \cdot L^{-1}$). The resulting units of measurement for K_d and R_d are ($L \cdot kg^{-1}$) or, in other words, (aqueous volume)/(sorbent mass) ratio. Hence, K_d and R_d are scaled neither to specific surface area nor to site density parameters and vary in many orders of magnitude at changing pH, total metal- or solid concentrations in the system. Instead, the GEM SCMs consider thermodynamic adsorption constants K made of surface concentrations C_j (density ratios like Γ_j/Γ_o, eqs 12A–F and 13). This result implies that at least the specific surface area $A_{\alpha,v}$ and molar mass of the sorbent $M_{\alpha,v}$ must be known for setting up any GEM SCM; accordingly, the experimental R_d values must be converted into surface concentrations and vice versa. If either or both of $A_{\alpha,v}$ and $M_{\alpha,v}$ are not determined (as for humates or ion-exchange resins) then the GEM SCM *sensu strictu* cannot be applied, although "work-arounds" may still be possible.

As in other SCMs, the GEM SCM is based on a *discrete set* of surface complexes (that is, binding constants) and, hence, there is no way to apply *distributions* of functional groups and adsorption constants. This limitation, however, is not as critical as it may seem. As Westall (1995) has shown, having four different binding constants is in practice sufficient for a formally good description of quite complex sorption isotherms on clay minerals or humic matter. In such a "semi-empirical" approach, one can fix the $\Gamma_{j,max}$ parameters and fit the "effective" adsorption constants K* on a single surface type. One can also assign surface complexes to different surface types (that is, provide $\phi_{\alpha,t}$ and $\Gamma_{t,max}$) and fit K* values using NEM or electrostatic SCM if appropriate. Finally, one can fix the K* values at the beginning (for instance, at 1, 10^2, 10^4, 10^6) and fit $\Gamma_{j,max}$ and/or $\phi_{\alpha,t}$ parameters. In the absence of any supporting crystallographic, micro-, and spectroscopic information, one cannot really prefer any of the three scenarios, which all turn into a "number-crunching game" not improving our understanding at all of the processes going on the mineral-water interface and not enhancing predictive capabilities of thermodynamic modeling.

If multi-site surface binding to "strong" and "weak" sites is to be modeled, it is important to realize that the SAT corrections with associated $\Gamma_{j,max}$ parameters must be foreseen for all "strong" surface complexes, otherwise the weaker surface complexes will have no chance to appear. The weakest surface complex usually does not require

SAT correction because its concentration will be limited either by chemical mass balance in the whole system or by surface precipitation (see fig.7 as an example). Hence, multi-site adsorption implies geometrically non-ideal behavior of at least the strongest surface complex, especially that of neutral stoichiometry or if the NEM is used.

Further, there is an ambiguity in using $\phi_{\alpha,t}$ and $\Gamma_{t,j,max}$ parameters to define "strong sites" on a multi-site-surface sorption phase in GEM SCMs for describing heterogeneous adsorption. One can assume that: (1) a given aqueous sorbate binds to specific surface sites of low density $\Gamma_{t,j,max} << \Gamma_o$ scattered over the whole mineral surface ($\phi_{\alpha,t} = 1$) or a major surface type ($\phi_{\alpha,t} >> 0$); or, alternatively, (2) the sorbate may bind to any site ($0 << \Gamma_{t,max} < \Gamma_o$) on localized surface patches of t-th type that occupy only a small fraction of the total mineral surface ($\phi_{\alpha,t} << 1$); such patches, however, develop their own EDL with properties different from those on other surface type(s) on the same sorbent. In both cases, a rather strong adsorption constant K is required to make most of the "strong" sites occupied before the aqueous sorbate starts binding onto the "weak" sites. The difference is, however, that in case (1), the concentration of the surface complex gets limited by a very strong non-competitive SAT $\Xi = f(\Gamma_{t,j,max})$, while in case (2), a much greater activity of the aqueous sorbate and its surface complex is required to obtain the necessary surface concentration (due to the factor $1/\phi_{\alpha,t}$, eq 13). Conversely, competition between sorbates is possible only in case (2), though at much weaker SAT corrections than would be required in case (1); the SCM of the surface type in case (2) will enter the geometrically non-ideal region at much more extreme conditions than that in the case (1). It is difficult to decide between these two cases in absence of microscopic or crystallographic information, quite important for a rigorous setup of alternative, mechanistically different models of heterogeneous surface complexation.

Next shortcoming of the present GEM SCM approach consists in not yet having a clear idea of how to implement the $1pK_A$ and CD-MUSIC EDL charge distribution models (Van Riemsdijk and Hiemstra, 1998 and references therein) well supported by spectroscopic data. The problem is twofold: first, one needs to establish (yet unknown) elemental stoichiometries of fractional-charge surface species or consider fractional charges in Coulombic EDL correction factors; second, one has to find out how the adsorption constants are related to $\phi_{\alpha,t}$ and $\Gamma_{t,j,max}$ parameters on heterogeneous mineral surfaces. More work here would be welcome, including GEM modeling of the experimental proton - ion adsorption stoichiometries. As discussed by Kulik (2000), the $2pK_A$ GEM TLM behaves to a large extent like the $1pK_A$ Stern model because the $>O_{0.5}H^o$ species is irrelevant in modeling titration data and can be omitted, and formal conversion from the remaining $>O_{0.5}^-$ and $>O_{0.5}H_2^+$ species to the $1pK_A$ species is possible.

The $O_{0.5}H$ stoichiometry of the neutral amphoteric surface functional group (sec. 2.3) is so far the only one used in $2pK_A$ GEM SCMs. It is certainly a limitation of the GEM approach, because alternative stoichiometries of functional groups are inferred to exist even on different planes of (hydr)oxide particle surfaces (Koretsky and others, 1998). In addition, the appropriate stoichiometries are yet to be found for surfaces of carbonate, sulfide, phosphate, and other minerals. Criteria for the selection of the optimal stoichiometries using spectro/microscopic or MD-modeling data need to be established. Application of Pauling bond valence principles to surface functional groups and complexes (Hiemstra and others, 1996; Van Riemsdijk and Hiemstra, 1998) might be very helpful in this respect.

At present, the GEM SCM approach can consider *sensu strictu* only monodentate surface species because of the way surface sites are counted in equations (13, 14, 29, 32 and 36). However, a variety of bidentate or polydentate mononuclear, binuclear, ternary surface complexes have been suggested in the literature, hence, the appropriate extensions would be desirable in the GEM approach also. It is possible to assign the same standard and reference states to mono- and polydentate surface complexes (analogous to aqueous species of different solvation). Alternatively, bidentate surface complexes can be formally converted into "quasi-monodentate" ones by multiplying their stoichiometry (and standard molal properties) by 0.5. Such procedures, however, most probably will lead to different SAT corrections at high surface coverages, but the related effects still remain unexplored. Likewise, the (non)-competitive SAT (eqs 29 and 32) reflect a simplest case of "Langmuirian" saturation of surface sites, assuming that no lateral interaction between surface complexes takes place and that the binding of a sorbate molecule blocks just one site, while the properties of adjacent surface species are not affected. This lack of interaction may not always be the case – for example, as assumed for the Frumkin-Fowler-Guggenheim (FFG) isotherm (Stumm, 1992). Obviously, much more work on elucidation of the functional forms and verification of SAT coefficients for surface complexes of different "dentateness" is necessary.

A multi-site-surface GEM SCM has already been applied for modeling surface acidity and REE sorption on illite (Kulik and others, 2000a). Reasonably good fits to titration data were obtained using a combination of the "amphoteric edge" surface types with properties of surface complexes on aluminol and silanol groups taken from that on alumina and silica surfaces, respectively, and the "permanent-charge basal plane ion exchange" surface types. The amphoteric edge surface types were modeled using TLM, and the "basal plane" surfaces – using NEM. The latter was constructed following a NEM of ion exchange on smectite clays by Fletcher and Sposito (1989). A pre-requisite of their model is that all the negative permanent-charge exchange sites (X^-) must be compensated either with metal cations or H^+ ions, to neutralize the charge. Thermodynamically, this results in log K > 7 of a binding reaction $X^- + Me^+ = X^-Me^+$. As ion exchange on X^- sites on clay minerals is usually not very selective, and maximum site density $\Gamma_{X,max}$ is not high (approximately 1 nm^{-2} for smectite to 3 nm^{-2} for illite basal planes), a strong competition must develop on such a surface type at elevated pH and high ionic strength, leading to very high values of competitive SAT for X^-Me^+ species and to rather stiff behavior of the GEM IPM algorithm. This behavior apparently contradicts the "outer-sphere," rather weak binding of the exchangeable aqueous cations, deemed to occur on the permanent-charge clay surfaces. Obviously, such behavior calls for the development of consistent SAT equations and electrostatic SCMs for permanent-charge ion exchange surfaces, using, for instance, the recent achievements of Kraepiel, Keller, and Morel (1999a,b).

The last example (Cr^{III} sorption on silica, sec. 3.3) demonstrates how easily (surface) precipitation can be handled in GEM approach together with the site heterogeneity and solubility of the sorbent. Unlike the LMA approach, the GEM IPM algorithm can always detect (in batch calculations) any point when a phase (single- or multi-component) must appear at equilibrium state (or disappear). Due to this capability, it seems that the GEM technique has an unmatched potential in thermodynamic modeling of the whole "sorption continuum" from outer-sphere surface complexation and permanent-charge surface ion exchange to heterogeneous incorporation of metals into "strong" sites/patches, surface (co)precipitation and, eventually, incorporation into the bulk sorbent.

As all these processes are kinetically-dependent and occur at different (increasing) time scales (Scheidegger and Sparks, 1996), the challenge in further model development lies in application of additional metastability constraints (eqs 3 and 4) derived from the experimental system characterization data. Further, kinetic concepts such as the "activated surface complex" theory (see Stumm, 1992) can be directly implemented into the time-dependent GEM SCM batch calculations. Since surface concentrations and speciation are computed at each (time) point, they can be used for setting dissolution/precipitation rates of the sorbent, thus enabling simulations on the basis of principles of local/partial equilibria. Kinetic constraints must also be applied in cases of metastable behavior of the mineral sorbent, for instance, in modeling adsorption from aqueous electrolyte on mineral particles at very low mineral dissolution rates at low temperatures (for example, hematite in suboxic/anoxic solutions).

CONCLUSIONS

1. A Gibbs energy minimization (GEM) technique for modeling equilibria involving surface complexation at mineral-water interfaces is presented, directly extending concepts of surface complexation modeling and the convex programming approach of Karpov, Chudnenko, and Kulik (1997). The stability of surface species is considered in terms of elemental stoichiometry, in a way similar to that for aqueous, gaseous, non-electrolyte liquid, and solid-solution substances. This treatment permits the modeling of systems in the sorption continuum "aqueous speciation - multi-site-surface complexation - surface (co)precipitation - solid solution" using bulk elemental stoichiometries, that is, *without adding balance constraints* $N_{t,s}$ *for surface sites.*

2. Thermodynamic relations introducing multi-site-surface complexation into GEM sorption phases include: (1) conventions on *standard and reference states for surface species* based on a reference density $\Gamma_o = 20\ \mu\text{mol} \cdot \text{m}^{-2}$; (2) definition of the concentration of a surface species as a ratio of its actual (state-of-interest) density Γ_j (μmol $\cdot$ m^{-2}) to Γ_o, leading to a general expression of activity (eq 13) that involves maximum site densities only through SAT corrections similar to activity coefficients; (3) expression of (electro)chemical potential (eq 14) that scales the quantity of the surface species to the quantity and specific surface area of the sorbent and includes Coulombic factor, if necessary; (4) activity/concentration relationships between aqueous sorbates and surface species, described by *surface activity term (SAT) corrections* $\Xi = f(\Gamma_j, \Gamma_{max})$; (5) reactive surface type (patch) area fractions ϕ_t for describing the surface heterogeneity.

3. Exclusion of the stoichiometry of the sorbent from the chemical formulae of surface species and functional groups should make their standard partial molal thermodynamic properties comparable for all (hydr)oxide surfaces. For the non-reacted neutral amphoteric surface functional group (≡OH, considered in 2pK_A surface complexation models), a stoichiometry $O_{0.5}H^o$ has been found (introduced by eq 38) with log K = 1.74436 and $G^o_{298}(>O_{0.5}H^o) = -128.55\ \text{kJ} \cdot \text{mol}^{-1}$.

4. It follows from equation (38) that the activity of the "surface solvent" $>O_{0.5}H^o$ depends only on activity of liquid H_2O but not on the concentrations of aqueous and surface complexes, quantity and composition of the sorbent. The non-reacted $>O_{0.5}H^o$ groups are thus macroscopically indistinguishable at different surface- and site types, and the site heterogeneity is only revealed in Γ_{max} values, charges, and thermodynamic properties of surface complexes, for instance, the $>O_{0.5}H_2^+$ species ("surface hydronium"); the $>O_{0.5}^-$ species ("surface hydroxyl"); and adsorbed cations or anions. G^o_{298} values of surface complexes can be directly fitted in GEM modeling of titration data, or converted to log K of the respective adsorption reaction (that includes $>O_{0.5}H^o$) using G^o_{298} values of other species.

5. The GEM SCM approach is illustrated by modeling literature potentiometric titration data for silica and rutile in NaCl electrolyte with the triple-layer (TLM), double-layer (DLM), and non-electrostatic (NEM) models using the GEM-Selektor code. Some examples were additionally calculated with the FITEQL3.2 code to demonstrate compatibility with other techniques. The last example (sorption of Cr^{III} on amorphous silica in $NaNO_3$ electrolyte) shows how easily the multi-site adsorption

and (surface) precipitation can be accounted for in GEM technique, and where the application of surface activity terms (SAT) cannot be avoided.

6. It was shown: (1) how approximate conversions between standard partial molal properties of surface complexes and their intrinsic adsorption constants can be done for different total site densities $\Gamma_C \neq \Gamma_o$ using equation (21), which makes refitting of titration data obsolete in many cases; (2) what the regions of "geometrically ideal" and "non-ideal" SCM behavior are and how they are controlled by the $\Gamma_{t,max}$ parameters via the surface activity terms (SAT, eqs 29, 32, and 36); and (3) why different EDL models and even sets of TLM parameters are not thermodynamically equivalent.

7. A strategy is suggested for fitting the "optimal" set of GEM TLM parameters, starting from experimental data selected at low surface loadings (or close to pH_{PZC}), then extending them to the whole titration intervals of pH and ionic strength, and, finally, setting $\Gamma_{t,max}$ parameters if surface heterogeneity or site limitations need to be introduced. In principle, this strategy can also be used with LMA codes by setting the total site density $N_{t,s}$ according to the reference site density Γ_o and implementing the SAT corrections $\Xi = f(\Gamma_{t,max})$.

The above findings create a sound basis for (re)consideration of a vast amount of published experimental data related to sorption equilibria on mineral-water interfaces, eventually leading to the compilation of a unified thermodynamic database for multi-site-surface complexation, internally consistent and comparable to existing databases for minerals, gases, and aqueous electrolyte.

ACKNOWLEDGMENTS

This paper is dedicated to Professor Igor K. Karpov in recognition of his outstanding contribution to geochemical thermodynamics. Stimulating discussions with S.U. Aja, B. Baeyens, U. Berner, M. Bradbury, G.W. Brümmer, W. Hummel, I.K. Karpov, R. Kretzschmar, J. Lützenkirchen, M.L. Machesky, A.V. Plyasunov, V.A. Sinitsyn, A.E. Scheidegger, G. Sposito, J. Tits, N.N. Vlasova, S.A. Wood and many other colleagues are gratefully appreciated. Special gratitude goes to M. Kersten, D.A. Sverjensky, E. Wieland, and two anonymous reviewers for their thoughtful and constructive comments on earlier versions of the manuscript, and to M. Bradbury for his generous help in improving the English style of the revised version. The author thanks J.C. Westall for providing the FITEQL3.2 code and T.S. Peretyashko for performing FITEQL calculations. This work was funded in part by the International Science Foundation (grants UAS000 and UAS200), the NAS/NRC (OCEE) Radwaste Program exchange grant (to S. Aja), the German Science Foundation (DFG), and the Swiss National Cooperative for the Disposal of Radioactive Waste (Nagra, Wettingen).

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