New aspects of thermodynamic sorption modelling introduced by Gibbs energy minimisation

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A unified thermodynamic model of the continuum 'ion exchange - adsorption - pore diffusion - surface (co) precipitation - solid solution', which would rationalise the most important interactions at mineral-water interfaces, still has to be developed. The closest to this goal is surface complexation approach, supported by many computer codes for iterative calculation of aqueous and surface speciation by the Law of Mass Action (LMA) algorithm (e.g. FITEQL3, MINTEQA2, PHREEQC). Alternative, Gibbs energy minimisation (GEM) techniques have also been developed (see Karpov *et al.*, 1997) and recently extended to include surface complexation on single-or multi-component solid phases (Kulik, 1995; Kulik and Aja, in preparation). Comparison of sorption modelling by LMA and GEM codes is given elsewhere (see abstract by Kulik and Peretyashko). In GEM formulation, the mass balance constraints are set for the total quantities of chemical elements (isotopes) in bulk composition plus one charge balance for the whole system, regardless of how many phases with sorption surfaces are included. This creates a new perspective in thermodynamic modelling, already explored for Nd and Eu sorption on clay minerals (Aja *et al.*, submitted, *Geochim. Cosmochim. Acta*; Kulik and Aja, in preparation), and for trace metal sorption onto non-stoichiometric Mn oxides (see abstract by Kulik and Kersten).

Recent development of GEM approach to surface complexation modelling highlighted some important theoretical issues which previously remained obscure. The present paper is aimed at discussing these new aspects in a hope to advance towards a unified thermodynamic description of sorption - solid solution - aqueous solution interactions.

Theoretical aspects

Sorption nanophase concept in GEM approach combines the end-members ($\geqslant 1$) of the solid carrier (sorbent) of certain specific surface area A and surface tension in pure water σ (if known) with surface species ($\geqslant 1$) on surface types ($\geqslant 1$), each occupying a prescribed effective fraction ϕ of the total surface area X_vA, where X_v is current number of moles of the sorbent. This permits to link the activity of a surface species to stability of the respective solid carrier without invocation of additional balance constraints. The ϕA product then serves as a state variable for a particulate or porous solid 'nanophase' which may exist at the equilibrium state.

Standard and reference states for surface components had to be reconsidered in GEM approach because of the need to find an exact form of (electro)chemical potential μ and reference level of partial molal Gibbs energy of formation from elements G^0, consistent to that for solids, gases and aqueous species. It has been found that the definition of the standard state must include a standard state specific surface area $A^0 = (\gamma^0 M)^{-1}$ (in m$\leqslant$ g^{-1}), where M is gram-formula mass of the solid carrier and γ^0 is conventional standard site density (20 µmol m^{-2} is suggested, the same for all surfaces). The reference state of a surface complex corresponds to zero EDL potential, infinitely low surface coverage and infinite dilution in aqueous electrolyte.

Activity/concentration relationships of surface species is the matter of a long discussion. In GEM approach, instead of the mass balance constraints on total number of reactive surface sites, a surface activity term λ (SAT) is introduced to suppress concentration of a surface complex when it approaches a physical limit defined by the maximum surface density γ_{max}. Three general SAT equations can be calculated: for competitive and non-competitive Langmuirian behaviour of surface complexes, and for the surface OH^0 group. The practical activity coefficient γ is reserved for all non-thermodynamic effects caused by the site discreteness, long-range electrostatic effects, inter-particle interactions, etc. Separate γ_{max} parameters can be set for calculation of competitive SAT on surface types and even for non-competitive SAT for single surface complexes. Now, the regions of ideal ($\lambda = 1$) and non-ideal ($\lambda > 1$) surface behaviour in the titration data can be identified for each sorbate, concentration of which is sensitive to γ_{max} in the non-ideal region only. This feature of GEM approach brings in an unmatched flexibility in modelling site/surface heterogeneity, particle- and solution-concentration effects. Using SAT concept, ion exchange on constant-charge surfaces can be treated as highly non-ideal competitive surface complexation with EDL electrostatic contribution cancelled out on the assumption that all sites are always occupied.

Towards a unified thermodynamic database for surface components

Stoichiometry and stability of surface OH^0 *group* is considered in GEM approach because known value of standard partial molal Gibbs energy $G^0(>OH^0)$ permits to convert surface deprotonation/complexation constants K_{a_1}, K_{a_2}, K_{SC} into consistent G^0 values of surface species at TP of interest. Stoichiometry of the sorbent may or may not be included (e.g. $[FeO]OH^0$ vs OH^0). The last choice is preferable, making G^0 values of surface species independent of composition and surface area of the sorbent. A simple iterative GEM procedure (Kulik, 1995) yields $G^0_{298}(OH^0) = -129544$ J mol^{-1} at $\gamma^0 = 20$ µmol m^{-2} and ambient conditions, insensitive to pH. For redox-dependent systems, another stoichiometry $O_{0.5}H^0$ is found, insensitive also to f_{O_2}, with $G^0_{298}(O_{0.5}H^0) = -128546$ J mol^{-1}. For the reaction $0.5H_2O_{aq} = {>}O_{0.5}H^0$, $\mathrm{Log}K = 1.744$ is found, independent of T and $P < 1$ kbar. Using pK^0_{a1}, pK^0_{a2}, pK^0_{SC} predicted or fitted for surface complexes at site density around $\gamma^0 = 12.05$ sites nm^{-2} (e.g. on TiO_2), the values of $G^0_{298}(SC)$ compatible for different surfaces or solid carriers could be calculated and utilised in GEM modelling of acidimetric and metal titration data. The modelled titration curves were insensitive to density of the 'non-reacted' $>OH^0$ groups; always, $\lambda_{>OH^0} \neq 1$ was needed to maintain the calculated total site density at prescribed γ_C or γ^0. Therefore, the ratio $\lambda_{>SC}/\lambda_{>OH^0} \neq 1$, and it decreases with increasing ΔpK_a even at pH_{ZPC}, contrary to common assumptions about surface complexation.

Influence of site density parameter Γ_C is one of the major sources of inconsistency in experimentally-derived surface acidity/ complexation constants. The GEM approach permits to demonstrate that, for any reaction involving $>OH^0$ group, pK_{SC} defined at γ_C transforms to pK^0_{SC} defined at γ^0 by a relation:

$$pK^0_{SC} = (sign)\log(\gamma_C/\gamma^0) + pK_{SC}, \qquad (1)$$

where (*sign*) depends on which side of the reaction the $>OH^0$ species stays. For the reactions with $>OH^0$ excluded, the fitted pK_{SC} are independent of γ_C, as long as all $\lambda_{>SC} = 1$. At high surface coverage ($\lambda_{>SC} \neq 1$), the fitted pK_{SC} for any kind of reaction should include SAT contribution, the stronger, the lower γ_C (or γ_{max}) is chosen. Thus, any SCM fits where low $\Delta pK_a < 4$ and high $C_1 > 2$ F m^{-2} were obtained, especially at $\gamma_C < 4$ sites nm^{-2} and/or $pH_{PZC} < 5.0$, appear to hide inconsistent model assumptions, probably ignoring the ion exchange or site heterogeneity phenomena, and should be considered cautiously or discarded for the purposes of predictive correlations of adsorption equilibrium constants.

References

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