Comparison of sorption modelling by Law of mass action (FITEQL) and Gibbs energy minimisation (Selektor-A) codes

D. A. Kulik
T. S. Peretyashko

Environmental Radiogeochemistry Centre (SSC ER), Palladin
Prosp. 34a, 252180 Kyiv, Ukraine

The Law of mass action (LMA) approach is traditional in calculating aqueous and surface speciation, supported by many computer codes such as MINEQL/FITEQL3.2 (Herbelin and Westall, 1996). Progress in development of an alternative, Gibbs energy minimisation (GEM) technique extended it to surface complexation on multi-component 'sorption nanophases' (see abstract by Kulik), as implemented in Selektor-A code (Kulik *et al.*, 1997). Since theoretical basis, numerical algorithms, input and output data are different in LMA and GEM, it is interesting to compare their efficiency with respect to sorption on mineral surfaces. This paper presents first results of comparative modelling of the same published data using FITEQL and Selektor-A codes, aimed at finding out whether identical results can be produced, the differences, and the extent of LMA and GEM complementarity. No fitting, only direct speciation was computed with FITEQL3.2.

Modelling techniques

In LMA formulation, mass balance is composed of master species (usually aqueous ions and surface OH^0 groups) plus charge balance constraints. For all derived species (complexes, minerals, gases, etc.), LMA expressions involving master species and reaction equilibrium constants K are taken into mass balance equations, which are then solved for concentrations of all species with the Newton-Raphson algorithm. Consequently, only *a priori* stable minerals can be included into mass balance. Speciation in both aqueous and solid solution phases can not be solved until the solubility product of solid mixture is supplied. Different redox states of the same element should be assigned to separate mass-balance constraints, with input-defined Eh. Surface complexes are treated similar to aqueous complexes, without a link to stability of the sorbent, but with additional mass-balance constraints for each surface site type.

In GEM formulation, all species are taken with their formal stoichiometry and arranged into single- or multi-component phases which may appear at equilibrium state. Mass balance is composed of total moles of chemical elements plus single charge balance constraint. For each species, a consistent value of apparent standard partial Gibbs energy of formation from elements $G^0_{T,P}$ must be provided at TP of interest. Appropriate non-ideality and surface parameters are set for phases. The output data of GEM include: equilibrium chemical potentials of chemical elements; quantities of species in all co-existing stable solid, liquid, aqueous, gaseous and sorption phases; equilibrium pH, pe (Eh) and partial pressures of gases; Karpov's criteria of stability for each phase and component. Since surface species are linked to 'solid carrier' end-members, the surface densities can be computed without additional mass balance constraints. Constant capacitance CCM, diffuse double layer DDLM (Dzombak and Morel, 1990), triple layer TLM (Hayes), and non-electrostatic NEM models can be applied separately on one to six surface types per solid sorbent. GEM requires highly consistent input thermodynamic and composition data, otherwise precision of mass balance may be limited.

LMA codes use $\mathrm{Log}K = f(T,P)$ for derived species only, while GEM - $G^0_{T,P}$ for all species in the system. However, Selektor-A is the only modelling code where the input data in thermochemical and reaction Log$K$ database formats are easily inter-converted and used together for calculation equilibrium states. This is important since no consistent thermochemical or EOS datasets are yet available for surface complexes.

Comparative model calculations

We ran FITEQL on some published TLM, CCM and DDLM fits for HFO (hydrous ferric oxide), TiO_2, SiO_2 and Al_2O_3 data. These LMA model titrations were reproduced with Selektor-A in two variants: (A) taking particular site density γ_{tot} as conditional standard state site density γ_C; (B) converting K_{a1}, K_{a2}, K_{SC} to conventional standard state site density γ^0

TABLE 1. Thermodynamic data (kJ mol^{-1})

Species	pK^{int}	G^{C}_{298}	pK^{0}	G^{0}_{298}
$>OH_2^+$	7.18	−166.23	6.46	−166.42
$>O^-$	8.82	−74.78	9.54	−75.09
$>OZn^+{}_w$	1.99	−261.10	2.71	−261.29
$>OZn^+{}_s$	−0.99	−268.97	1.34	−269.16
$>OH^0$		−125.19		−129.54

= 20 μmol m^{-2} (see abstract by Kulik). Cases A and B require different procedures for finding molal Gibbs energies of surface species, as illustrated below on a numerical example of surface acidity and two-site Zn adsorption on HFO at $T = 25$ °C and $P = 1$ bar. Thermodynamic data for aqueous, gaseous and mineral species in the system Fe-Zn-Na-Cl-Ar-H-O were taken from Selektor-A database. Bulk composition was 1 kg of H_2O; 1 g of model air; 0.1 *m* NaCl; 0.09 g FeOOH (A = 600 m^2 g^{-1}, γ_{tot} = 2.31 sites nm^{-2}). NaOH was used as a titrant. DDLM pK_{a1}, pK_{a2}, pK_{SC} were taken from (Dzombak and Morel, 1990) and FITEQL3.2 examples.

(1) G^{0}_{298} of $>OH^0$, $>OH_2{}^+$, $>O^-$ and weak $>OZn^+_w$ surface species for the conditional state at γ_C = 3.84 μmol m^{-2} were iteratively adjusted in GEM equilibria calculations at pH = 8.0 (pH_{PZC}) using pK^{int} values (Table 1), until correct γ_{tot} was calculated. This was done also for G^{C}_{298} of a strong $>OZn^+_s$ species for another conditional state at $\gamma_{C,s}$ = 0.094 μmol m^{-2}. Acidimetric HFO titration from pH 3 to 13 was simulated as a sequence of inverse titration GEM problems at $Zn_{tot} = 10^{-6}$ *m*, first with all surface activity terms (SAT) $\lambda = 1$. In this ideal adsorption model, surface densities were correct at 6.5 < pH < 9.5, with large over-prediction for $>OH_2{}^+$ at pH < 6.0 and for $>O^-$ at pH > 10.0. Next, γ_{max} = 3.84 μmol m^{-2} was set for $\lambda_{>OH0}$, competitive $\lambda_{>OH2+}$, $\lambda_{>O-}$, $\lambda_{>OZn+w}$, and γ_{max} = 0.094 μmol m^{-2} - for the non-competitive $\lambda_{>OZn+s}$. The non-ideal GEM model produced the same surface speciation as in FITEQL run (Fig. 1).

(2) pK^{int} were converted to standard state pK^0 at γ^0 = 20 μmol m^{-2} by adding $\delta pK = -\log[\gamma_{max}/\gamma^0]$ = 0.72 (for $>OZn^+_s$, $\delta pK = -\log[0.094/20.0] = 2.33$), and G^{0}_{298} values were calculated from pK^0 and known

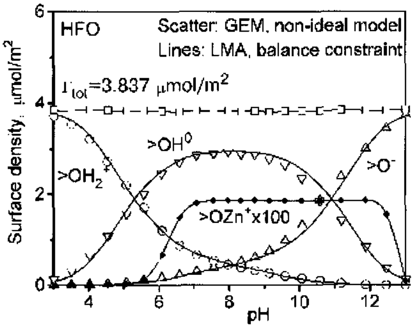

FIG. 1. Comparison of GEM and LMA calculations.

$G^{0}_{298}(>OH^0)$ (see Table 1). After re-running the titrations, only computed density of $>OH^0$ was different. The same curves as in (1) were obtained for surface complexes in both ideal and non-ideal models, which is not surprising as $G^{C}_{298} - G^{0}_{298}$ = 0.19 kJ mol^{-1} only (except $>OH^0$).

Conclusions

LMA mass balance constraint on total site density is equivalent to a conditional standard state at $\gamma_C = \gamma_{tot}$ plus competitive SAT corrections in GEM approach. ΔpK_a is proportional to γ_C. The model $>OH^0$ group does not compete with surface complexes. G^{0}_{298} of surface complexes appear to be independent of the particular standard site density (γ_C or γ^0), as well as pH_{PZC} and K^{0}_{ads} of reactions where $>OH^0$ was excluded. At low coverage, all SCMs work in ideal region. TLM with $\Delta pK_a > 5$ enters the non-ideal region at relatively high solution concentrations and thus seems to be thermodynamically preferable over CCM or DDLM.

References

Dzombak, D.A., and Morel, F.M.M. (1990) *Surface complexation modeling (HFO)*. Wiley, NY.

Herbelin, A. and Westall, J.C. (1996) *FITEQL3.2 User's Manual*. Corvallis, OR.

Kulik, D.A., Dmitrieva, S.V., Chudnenko, K.V. *et al.* (1997) *Selektor-A 3.1*β User's Manual. Kiev.