Groundwater

Guest Editorial/

Flying Blind: Geochemical Modeling and Thermodynamic Data Files

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For geochemical modeling, successful code development over the last 30 years has enabled wide applications. However, an explosion of applications has been accompanied by "institutionalized black boxing," a term used by Anderson (1983) to warn of the detrimental consequences of the widespread use of solute transport models without adequate training. We refer to this practice as "flying blind." For example, popular software packages such as PHREEQC, visual MINTEQ, TOUGHREACT, and The Geochemist's Workbench® have large user communities (any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government). However, prominent geochemists have published in premier geochemical journals with reference to the "PHREEQC model," or the "MINTEQ model" of aqueous speciation or mineral solubility, without mentioning what thermodynamic data were used in the modeling. We remind readers that a computer "code" is NOT a "model" (Nordstrom 2012) and that many different models are used within the same code.

For geochemical modeling, a thermodynamic data file (TDF) must accompany an input file and the executable code, comprising the "rule of three" (Zhu and Anderson 2002). A TDF provides equilibrium constants for reactions involving solids, aqueous species, gases, adsorbed surface species, and ion-exchange species. A TDF may also provide parameters for modeling kinetics of mineral dissolution and precipitation, activity coefficients of aqueous species, and fugacity coefficients of gaseous species. The quality of geochemical modeling results depends on the quality of the TDF.

A basic requirement for a reliable TDF is internal consistency (Helgeson et al. 1978). Internal consistency implies, at a minimum, that the thermodynamic relationships, reference and standard states, and activity coefficient models are consistently applied to all data within a given TDF. Taking thermodynamic and kinetic data from one source and merging them with data from another source without ensuring they are internally consistent leads to degraded results (Nordstrom and Munoz 1994).

As of June 2022, the PHREEQC package (v.3.7.3) contained 13 TDFs and the user can also develop their own TDF. This structure is helpful because different TDFs can serve different applications. However, calculated speciation, mineral solubilities, and gas concentrations may vary substantially. Each TDF also has its own limits of applicability in terms of temperature, pressure, salinity, and chemical composition. It is the user's responsibility to ensure the reliability of the TDF for the given application. The TDF used should be cited, documented, and justified, keeping in mind that current research continues to explore limitations and make improvements to TDFs.

The proliferation of geochemical modeling applications coincides with the disappearance of thermodynamics courses in Earth Science curricula. It has been our experience that a change in student interest, faculty expertise, and enforcement of minimum enrollment at some universities have largely disabled the regular offering of these courses at most institutions. Automated software capabilities of computing and graphing cannot be a substitute for the user's basic background and training in thermodynamics, chemical kinetics, interfacial processes, and hydrogeochemistry.

Journals like *Groundwater* can address these concerns by requiring authors to state clearly which TDFs were used with geochemical codes. Because most of these databases can be modified, another useful requirement would be to provide a listing of the key thermodynamic, kinetic, and surface data that are responsible for the modeling results. Such detail could be released in appendices or online Supporting Information files. For papers with complex geochemical models, putting the used TDF in a repository, consistent with *Groundwater*'s data sharing policy, would be beneficial. Organizations such as NGWA and CUASHI could also offer training short courses and

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summer schools in thermodynamics and database evaluation to mitigate this problem.

Flying blind with geochemical modeling is easy. Producing useful and high-quality modeling results takes time, dedication, and effort and is the least we can do to honor those modeling pioneers who showed us the path forward.

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