Evaluation of uncertainties in solid–aqueous–gas chemical equilibrium calculations

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ABSTRACT

Thermodynamic calculations are traditionally carried out under the assumption of specified input parameters. Errors associated to the results are not often estimated. Here, we propose a novel algorithm that propagates the uncertainty intervals on thermodynamic constants to the uncertainty in chemical equilibrium compositions. The computing uses a dataset of uncertainties on thermodynamic parameters for minerals, solution species and gases consistent with the SUPCRT92 database. Also the algorithm of nonlinear optimization is thoroughly described and realized on a base of the CRONO software. This code can be incorporated into reactive mass transport models as a core for calculating equilibrium compositions. The performance of the algorithm is tested in an experimental system involving Mont Terri's Opalinus Clay interacting with pore water. Its effectiveness is also evaluated against Monte Carlo simulations and Latin Hypercube sampling.

1. Introduction

Progresses in thermodynamic modeling allowing the higher confidence in calculated data can be achieved with measures of uncertainty in computational simulations. Currently, the most popular thermodynamic modeling codes, such as PHREEQC (Parkhurst and Appelo, 1999), CrunchFlow (Steefel, 2001), HCH (Shvarov, 2008), GEOCHEQ (Mironenko et al., 2008), Geochemist's Workbench (Bethke and Yeakel, 2012), produce results that neglect the impact of the ambiguity associated with input thermodynamic parameters. Possibly, the only exception is the GEMS-PSI software (Kulik et al., 2004), which includes the GEMS UnSpace module and provides sensitivity analysis about the impact of input data uncertainty on calculated equilibrium compositions (Chudnenko et al., 2004; Chudnenko, 2010). The contemplation of uncertainty intervals can potentially provide new insights into simulation algorithms, outline chemical transformations in the studying systems and increase the value of thermodynamically based models.

The problem of uncertainty traditionally challenges thermodynamic computation. Monte Carlo-based approaches have been tested by a number of researchers (Anderson, 1976; Schecher and Driscoll, 1987, 1988; Nordstrom and Ball, 1989; Criscenti et al., 1996; Whiting et al., 1999). Unlike the single calculation at a certain mode of input data, the Monte Carlo method demands numerical calculations of hundreds to several thousands of chemical equilibrium compositions (Chudnenko, 2010), requiring large computation time. This is why the use of the method in thermodynamic modeling has declined. The GEMS UnSpace module, in its turn, demands 101–2000 calculations of equilibrium (Chudnenko, 2010). It does not use the random distribution of input parameters, but propose the usage of equal apportionment of testing points into a n-dimensional space of uncertainties, so called the hypercube. This allows reducing the number of equilibrium calculations significantly, outperforming the classic Monte Carlo method.

In this work, we propose an alternative, novel algorithm to estimate the impact of input thermodynamic parameters uncertainties to the predicted composition of a system. The maximal difference in the chemical composition of a system can be found by the maximization of the Gibbs–Durham function, considering a constrained n-dimensional space of input uncertainties on Gibbs free energies. In numerous cases, the resulted intervals of uncertainty can be estimated by 5 equilibrium calculations only and not exceeding $20n + 5$, where n is a number of components of the considering system. The algorithm operates within the CRONO software (Novoselov and Souza Filho, 2013). This code can be applied separately or as an equilibrium computation core in complex geochemical models.

The demonstration database of thermodynamic constants stems from the latest revision (slop07.dat) of SUPCRT92 (Johnson

et al., 1992) and includes minerals, solution species and gases within the framework of the O-H-Al-C-Ca-Cl-F-Fe-K-Mg-Mn-N-Na-P-S-Si-Ti system (Appendix 1). According to the data format of SUPCRT92, the properties of minerals, aqueous species, and gases are considered below in terms of the following unit conventions: temperature in Kelvin ($°K$), pressure in bar, energy in thermo-chemical calories (cal, 1 cal=4.184 J), mass in moles (mol), and volume in cubic centimeters (cm^3).

2. Uncertainties on thermodynamic parameters

2.1. Estimation of ambiguity in apparent Gibbs free energies of minerals

Calculation of equilibria is based on Gibbs free energy at defined temperature and pressure ($G^0_{T,P}$, cal mol^{-1}). Uncertainties of those parameters can potentially impact the results. They are derived from uncertainties on apparent standard Gibbs energy of formation ($G^0_{T_r,P_r}$, cal mol^{-1}), entropy ($S^0_{T_r,P_r}$, cal mol^{-1} $°K^{-1}$), isobaric standard molar heat capacity ($C^0_{P_r}$, cal mol^{-1} $°K^{-1}$) and standard molar isobaric volume ($V^0_{T_r,P_r}$, cm^3 mol^{-1}), which can be converted to cal mol^{-1} bar^{-1} dividing by 41.84 (Helgeson et al., 1978):

$$G^0_{T,P} = G^0_{T_r,P_r} - S^0_{T_r,P_r}(T - T_r) + \int_{T_r}^{T} C^0_{P_r} dT - T \int_{T_r}^{T} \frac{C^0_{P_r}}{T} dT$$
$$+ \int_{P_r}^{P} V^0_{T_r,P_r}/41.84 dP \tag{1}$$

where $T_r = 298.15°K$ and $P_r = 1$bar. Integration of Eq. (1) yields SUPCRT92's equation of Gibbs free energy for mineral species (e.g., Oelkers et al., 2009; Aradóttir et al. 2012):

$$G^0_{T,P} = G^0_{T_r,P_r} - S^0_{T_r,P_r}(T - T_r) + a\left(T - T_r - T \ln\left(\frac{T}{T_r}\right)\right)$$
$$- \left(\frac{(c + bT_r^2 T)(T - T_r)^2}{2T_r^2 T}\right) + V^0_{T_r,P_r}(P - P_r)/41.84 \tag{2}$$

where a (cal mol^{-1} $°K^{-1}$), b (cal mol^{-1} $°K^{-2}$) and c (cal mol^{-1} $°K^{-1}$) are Maier–Kelly heat capacity fitting coefficients for the specified mineral from T_l to T and the heat capacity equals to:

$$C^0_{P_r} = a + bT + cT^{-2} \tag{3}$$

Following Bevington and Robinson (2003), if the dependent variable x is related to the sum of uncertainty-bearing parameters y and z:

$$x = Yy + Zz \tag{4}$$

where Y and Z are corresponding multipliers, then the resulted uncertainty σ_x is given by:

$$\sigma_x = \sqrt{(Y\sigma_y)^2 + (Z\sigma_z)^2 + 2YZ\sigma_{yz}^2} \tag{5}$$

In the case y and z are not related measurements, σ_{yz} equals to 0. Therefore, the propagation of errors of apparent standard Gibbs energy of formation, entropy, heat capacity and molar volume to $G^0_{T,P}$ for minerals can be calculated from Eq. (2), as follows:

$$\sigma_{G^0_{T,P,i}} = \left(\begin{array}{l} \left(\sigma_{G^0_{T_r,P_r,i}}\right)^2 + \left((T - T_r)\sigma_{S^0_{T_r,P_r,i}}\right)^2 + \left(\left(T - T_r - T \ln\left(\frac{T}{T_r}\right)\right)\sigma_{a\,i}\right)^2 \\ + \left(\left(TT_r - 0.5T^2 - 0.5T_r^2\right)\sigma_{b\,i}\right)^2 + \left(\frac{(T^2 - 2TT_r + T_r^2)}{2T_r^2 T}\sigma_{c\,i}\right)^2 \\ + \left((P - P_r)/41.84\sigma_{V^0_{T_r,P_r,i}}\right)^2 \end{array} \right)^{\frac{1}{2}} \tag{6}$$

where $\sigma_{G^0_{T,P,i}}$, $\sigma_{G^0_{T_r,P_r,i}}$, $\sigma_{S^0_{T_r,P_r,i}}$, σ_a, σ_b, σ_c, and $\sigma_{V^0_{T_r,P_r,i}}$ are sigma values of the corresponding thermodynamic parameters of the solid phase i. Although some recent reports of thermodynamic observations provide listed uncertainties (Fridriksson et al., 2001; Gailhanou et al., 2012, 2013), SUPCRT92 does not refer those parameters, including its latest version. Therefore, uncertainties themselves are challenging to assess.

Most constants of mineral species in SUPCRT92 were derived from the dataset published by Helgeson et al. (1978). Whereas those authors considered the validity of the thermodynamic data, they concluded only that in most cases such uncertainties for $G^0_{T_r,P_r}$ are in the order of a hundred cal mol^{-1} or less. The lack of uncertainties assigned to the thermodynamic properties of SUPCRT92 can be complemented by means of comparison with alternative datasets. A database of thermodynamic parameters containing their uncertainty intervals was proposed by Robie et al. (1979), and later revised by Robie and Hemingway (1995). This set of constants stems generally from the same data sources employed by Helgeson et al. (1978) and contains a lot of coincidences. Uncertainties for mineral species can also be found in the database reported by Holland and Powell (1998, 2011). Those datasets include uncertainty data in distinct formats and demands to be recalculated to sigma values. Robie and Hemingway's (1995) compilation provides 2σ uncertainty interval; whereas Holland and Powell (1998) catalogs report 95% confidence interval or 1.97σ. Gailhanou et al. (2012, 2013) report uncertainties on $G^0_{T_r,P_r}$ as sigma values, but entropy and heat capacity are provided as deviations maxima. Maximal errors considered in Fridriksson et al. (2001), Jenkins and Bozhilov (2003), Vieillard et al. (2004) and Gailhanou et al. (2012, 2013) seem to correspond to 3σ values. The calculated values of Gibbs free energy ($G^0_{T,P}$) with their uncertainty intervals ($\sigma_{G^0_{T,P}}$) at 25 °C and 1 bar are shown in Fig. 1 for selected minerals. The level of agreement is very encouraging and shows that the uncertainties reported in Robie and Hemingway (1995) and Holland and Powell (2011) can be joined with SUPCRT92 data.

The propagation of errors at elevated temperatures and pressures demands especial consideration. According to Eq. (6), the growing pressure enhances the resulted ambiguity of Gibbs free energy through the uncertainty of standard molar isobaric volumes. Those parameters are referred in Robie et al. (1979) and Robie and Hemingway (1995). Therewith, the uncertainties of entropy and heat capacity impact the resulted uncertainty intervals with increasing temperature. Although there are a number of compilations (e.g., Robie and Hemingway, 1995) specifying those parameters for entropy, the uncertainties on heat capacity or Maier–Kelly coefficients for distinct mineral species can be found only in a limited number of sources (e.g., Hemingway and Sposito, 1989; Vieillard et al., 2004; Gailhanou et al., 2012, 2013). To compare the relative impact of uncertainties on $S^0_{T_r,P_r}$, $C^0_{P_r}$, and $V^0_{T_r,P_r}$ at elevated T and P, we calculated the corresponding terms of Eq. (5) and plotted them in Fig. 2.

Fig. 2 shows that the propagated errors of Gibbs free energies depend much less in entropy, heat capacity and molar volume uncertainties than on $G^0_{T_r,P_r}$ ambiguities. The uncertainty interval of entropy for chlorite (Robie and Hemingway, 1995) can increase the calculated uncertainty up to 26%, whereas the impact of other