Improvements in Internal Consistency of Inorganic Thermodynamic Data at 298.15 K

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Improving the internal consistency of thermodynamic data has been a long-term need since the beginning of the 20th century. Among the several requirements for internal consistency, the most challenging is consistency among different techniques as well as different investigations using the same technique. The basic laws and equations of thermodynamics require that results from calorimetry, conductivity, solubility, electrochemistry, and isopiestic techniques should all converge on the same thermodynamic values of any given system. In addition, when building a network of interconnected thermodynamic properties there is the question of where best to start the network if using a sequential approach (e.g., the "NBS Tables," Wagman et al., 1982) or whether to proceed with simultaneous regression (e.g., the CODATA calcium book, Garvin et al., 1987). Both have advantages and disadvantages. In fact, both references used both approaches.

A weakness with the sequential approach is that a serious error in the early part of the sequence is propagated through the chain and the results are not representative of the overall inherent errors. A weakness with simultaneous regression is that it is not always possible to assign representative weights to data because method information is unavailable, and without accurate error estimates the results can be skewed towards data of higher uncertainty. Furthermore, only a selected data subset can be reasonably fitted simultaneously. Both approaches require a thorough screening of the literature which is also tedious and time-consuming.

In this report, three examples are described of internal consistency evaluations for thermodynamic properties of aqueous speciation and solids of inorganic reactions of particular importance to geochemistry at reference conditions of 298.15 K and 0.1 MPa. The first is a network of minerals and aqueous species involving arsenic (Nordstrom et al., 2014) and begins with electrochemical cell measurements of arsenolite, As_2O_3(cubic). The second is a network involving the solubilities of three fluoride-bearing minerals, fluorite, CaF_2, cryolite, Na_3AlF_6, and villiaumite, NaF. Villiaumite solubility and mean activity coefficient is well-characterized which can be combined with the well-characterized free energies of the aqueous ions to improve the free energy of villiaumite. The third is a single reaction, the second dissociation constant of sulfuric acid, for which mean values for enthalpy, heat capacity, entropy, and log K_{sp} have been compiled from the literature (Hefter and Gumiński, 2019) and used to derive a temperature-dependent equation that compares well with literature data for 273.15 to 647.10 K. The results are also tied to the CODATA values for SO_4^{2-}(aq) leading to a slight improvement in the properties of HSO_4^-(aq). In each example a well-characterized substance or reaction provided a starting point or anchor for a wider network of related substances and reactions.

References

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