ThermAP predictive model: overview

ThermAP – standing for "Applied Predictive Thermodynamics" – is a predictive thermodynamic calculation program developed by Christophe Drouet at CIRIMAT-CNRS Toulouse, France. Its web-design was elaborated by Pierre Alphonse. *ThermAP* aims at estimating the standard entropy S°, formation enthalpy $\Delta H_f°$ and Gibbs free energy $\Delta G_f°$ of families of complex oxides (from the elements taken in their standard state, typically at 298K/1bar).

It is based on an additive "contributive" methodology, where each constituting ion "i" in the compound chemical formula is associated to an entropy s(i), enthaly h(i) and Gibbs free energy g(i) contribution term evaluated to fit accessible experimental data by minimization of the relative total error. In this model, these contributions are directly related to the thermodynamic properties of the corresponding simple oxides (e.g. CaO in the case of Ca^{2+}) via the application of "correcting" factors that are assessed in the model. This approach was inspired from preliminary works from the literature on contributive thermodynamics (e.g. La Iglesia *et al.*). However, in *ThermAP*, several optimizations/improvements have been made in the design and comprehension of the energetic contributions of each ion in a given subfamily of compounds. The model was particularly explored in terms of Gibbs free energy and entropy, therefore allowing also enthalpy assessments; and direct correlations were unveiled between the corrective factors and the nature of the considered elements. The element's electronegativity and the affinity of cations for oxygen were found to be particularly influential factors. These findings then allowed extrapolations, for similar compounds incorporating other substituting ions for which no experimental data was yet accessible, thus allowing one to derive estimates of their thermodynamic properties. *ThermAP* also proved helpful to estimate $\Delta G_f°$, $\Delta H_f°$ and S° of solid solutions with varying substituents' natures and amounts, including nonstoichiometric ones, and even considering the effect of hydration.

This approach may prove helpful for speciation calculation software (PHREEQC®, Minteq®…), in mineralogy (terrestrial, Martian…), hydrometallurgy, environmental sciences (e.g. for the remediation of polluting ions), in biomaterials science (e.g. doping of bioceramics with substituting bioactive ions), and many other domains where the conditions of formation/dissolution/evolution of complex oxides need to be determined and taken into account.

The T*hermAP* model was first initiated with phosphate apatite compounds, and its basis was laid in the initial publication: ***Drouet et al., The Journal of Chemical Thermodynamics, 81 (2015) 143-159, doi:10.1016/j.jct.2014.09.012***. The model has then been expanded to other complex oxides, and other publications have been dedicated to further developments of *ThermAP*, which has started to be used by several international researchers. Several databases are included in the software, dedicated to several mineral types, and additional databases will be added regularly.

The software is **free of use** provided that its use is mentioned in any published outcomes in the form: "these calculations were carried out using the *ThermAP* program (Drouet C, Alphonse P. *ThermAP* additive model for applied predictive thermodynamics, www.christophedrouet.com/thermAP).

Good calculations! (and do not hesitate to contact the author for suggestions or comments).

Chris Drouet.