

STANDARD ENTROPY AND ENTHALPY VALUES FOR PETROLOGICAL CALCULATIONS: RESULTS FROM RELAXATION CALORIMETRY AND FROM DENSITY FUNCTIONAL THEORY

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Relaxation calorimetry (RC) is a relatively new experimental method that enables the measurement of low-temperature heat capacities (C_p). Its commercial implementation is the physical properties measuring system (PPMS) from Quantum Design®. A major advantage of RC is that *small sample amounts in the mg range* can be studied as compared to other calorimetric techniques that require at least several grams of material (e.g. adiabatic calorimetry). RC thus opens up a new field for measuring low-T C_p for the first time on many phases that can only be synthesized in small amounts in high-pressure devices or occurring in nature as small or fine-grained crystals. For handling powdered samples, specific techniques have been developed.

The impact of RC on petrologic thermodynamic calculations is twofold:

- Mineral end members: *The standard entropy S^0 can now be determined* with an accuracy of 0.7-1.0%. Examples that will be discussed include the garnet end members spessartine and andradite and the biotite end members annite and eastonite.
- Solid solutions: PPMS measurements made on solid solutions allow the *calorimetric excess entropy* to be determined. Examples that will be discussed are garnet and feldspar solid solutions, as well as the (Li,Na)FeGe₂O₆ pyroxene solid solution.

The enthalpy of formation (usually from the elements), $\Delta H_{f,elements}^0$, is another important thermodynamic quantity required in petrological calculations. It is either measured via some solution calorimetric method, or derived from phase equilibrium experiments resulting in an internally consistent thermodynamic data set. As will be shown by BENISEK & DACHS (in prep.) calculations using density functional theory (DFT) can be another useful source for gaining reliable $\Delta H_{f,elements}^0$ values. The new procedure requires (a) the computation of the enthalpy of formation of a specific phase from the oxides, $\Delta H_{f,oxides}^0$, using DFT and (b) the conversion of this value to a corresponding $\Delta H_{f,elements}^0$ based on $\Delta H_{f,elements}^0$ values of the oxides taken from published literature (e.g. an internally consistent thermodynamic data set or JANAF tables). DFT calculations testing this method have been made for aluminosilicates, feldspars, garnets, olivines, pyroxenes, layer silicates, perovskite and amphibole. The so calculated $\Delta H_{f,elements}$ values of relevant end members do not deviate more than 1 % from reference values, most agree to within 0.5 %. This method thus seems to be a new promising tool for calculating $\Delta H_{f,elements}$ values of petrologically relevant mineral end members, especially in cases where experimental data are lacking or the end member in question does not exist physically, because the compositional range is restricted to the solid solution (e.g. eastonite in the case of the biotite solid solution).