Letter

A simple method for obtaining heat capacity coefficients of minerals

Samuel Bowman1,*, Arkajyoti Pathak1, Vikas Agrawal1, and Shikha Sharma1

1Department of Geology and Geography, West Virginia University, Morgantown, West Virginia 26506, U.S.A.

Abstract

Heat capacity data are unavailable or incomplete for many minerals at geologically relevant temperatures. Despite the availability of entropy and enthalpy values in numerous thermodynamic tables (even sometimes at elevated temperatures), there remains need for extrapolation beyond, or interpolation between, temperatures. This approach inevitably results in estimates for entropy and enthalpy values because the heat capacity coefficients required for optimal thermodynamic treatment are less frequently available. Here we propose a simple method for obtaining heat capacity coefficients of minerals. This method requires only the empirically measured temperature-specific heat capacity for calculation via a matrix algorithm. The system of equations solver is written in the Python computing language and has been made accessible in an online repository. Thermodynamically, the solution to a system of equations represents the heat capacity coefficients that satisfy the mineral-specific polynomial. Direct coefficient calculation will result in more robust thermodynamic data, which are not subject to fitting uncertainties. Using hematite as an example, this method provides results that are comparable to conventional means and is applicable to any solid material. Coefficients vary within the traditional large 950 K temperature interval, indicating that best results should instead utilize a smaller 400 K temperature interval. Examples of large-scale implications include the refinement of geothermal gradient estimation in rapidly subsiding sedimentary basins or metamorphic and hydrothermal evolution.

Keywords: Gaussian elimination, heat capacity, hematite, system of equations

Introduction

Earth systems are rarely, if ever, truly at standard temperature and pressure; the effect of these parameters must be considered for robust thermodynamic treatment. Regarding systems at non-standard temperatures, mineralogists and petrologists employ (directly or indirectly) the heat capacity (Cp) for the selected material(s) for purposes such as studying the effects of temperature and pressure for basin modeling or maturity modeling (Waples and Waples 2004). However, despite the wide availability of Cp data for many minerals, in most cases the numbers are often applicable to narrow temperature ranges. In other cases, the entropy (∆S) and enthalpy (∆H) must either be extrapolated or interpolated to the desired temperature (Robie and Hemingway 1995), or the final free energy (∆G) is obtained via linear regression (Toulmin and Barton 1964). Considering that Cp follows a polynomial trend for temperature, it is expected that linear regressions of free energy may introduce uncertainty (although linear behavior may provide reasonable estimates for free energy using small ∆T intervals). One limitation within the present heat capacity literature may be found for the mineral hematite in Hemingway (1995), where there is a function discontinuity occurring at 950 K between the lower (T <950 K) and upper (T >950 K) temperature domains. The heat capacity of a solid is typically continuous except for occasional discontinuities and has been attributed to crystallographic/phase transitions (e.g., Guyot et al. 1993). Heat capacity function discontinuities will be translated to the calculated or regressed polynomial coefficients. Ideally, the characteristic mineral specific Cp coefficients have been determined and published, allowing for exact calculation of entropy and enthalpy at a given temperature. Unfortunately, these coefficients are often unavailable throughout the literature, one notable exception being the compilation in Robie and Hemingway (1995).

Fundamentally, the heat capacity of a material is effectively the input energy required to raise the thermal energy of that same material. The heat capacity is vital to mineralogical, petrological, and geochemical research. It is quantified for a selected material using various calorimetric techniques and when plotted against temperature, takes the form of a polynomial (e.g., Klemme and van Miltenburg 2003; Benisek et al. 2012). The Cp polynomial order and the number of coefficients varies throughout the literature. For example, the form in Xiong et al. (2016) contains seven coefficients and is a third-order polynomial, while the Shomate equation (e.g., NIST) has five coefficients and is also a third-order polynomial, while the progenitor, the Maier-Kelley form contains only three coefficients and is a second-order polynomial (Maier and Kelley 1932). The form commonly found associated with geological solids or minerals is the second-order polynomial with five coefficients, as given by Hemingway et al. (1978). Finally, the Cp polynomial formula is often determined by regression of existing data to fit a specific polynomial form (Hemingway 1990; Waples and Waples 2004). The primary goal of this study is to evaluate the polynomial through direct means. This