Heat capacity of minerals in the system Na₂O – K₂O – CaO – MgO – FeO – Fe₂O₃ – Al₂O₃ – SiO₂ – TiO₂ – H₂O – CO₂: representation, estimation, and high temperature extrapolation

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Abstract. A revised equation is proposed to represent and extrapolate the heat capacity of minerals as a function of temperature:

\[ C_p = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3} \] (where \( k_1, k_2 \leq 0 \)).

This equation reproduces calorimetric data within the estimated precision of the measurements, and results in residuals for most minerals that are randomly distributed as a function of temperature. Regression residuals are generally slightly greater than those calculated with the five parameter equation proposed by Haas and Fisher (1976), but are significantly lower than those calculated with the three parameter equation of Maier and Kelley (1932).

The revised equation ensures that heat capacity approaches the high temperature limit predicted by lattice vibrational theory \( (C_p = 3R + \frac{\alpha_2}{VT^2}) \). For 16 minerals for which \( \alpha \) and \( \beta \) have been measured, the average \( C_p \) at 3,000 K calculated with the theoretically derived equation ranges from 26.8±0.8 to 29.3±1.9 J/(afu·K) (afu = atoms per formula unit), depending on the assumed temperature dependence of \( \alpha \). For 91 minerals for which calorimetric data above 400 K are available, the average \( C_p \) at 3,000 K calculated with our equation is 28.3±2.0 J/(afu·K). This agreement suggests that heat capacity extrapolations should be reliable to considerably higher temperatures than those at which calorimetric data are available, so that thermodynamic calculations can be applied with confidence to a variety of high temperature petrologic problems.

Available calorimetric data above 250 K are fit with the revised equation, and derived coefficients are presented for 99 minerals of geologic interest. The heat capacity of other minerals can be estimated (generally within 2%) by summation of tabulated ‘oxide component’ \( C_p \) coefficients which were obtained by least squares regression of this data base.

Introduction

Knowledge of the heat capacity of minerals is fundamental to the description of their thermodynamic behavior. While heat capacity can be determined by a variety of calorimetric techniques, adequate representation of these data as a function of temperature is necessary to provide for interpolation between the temperatures of the calorimetric measurements.

Table 1: Heat Capacity Equations

<table>
<thead>
<tr>
<th>Source of Equations</th>
<th>Terms in ( C_p ) Equations</th>
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</thead>
<tbody>
<tr>
<td>Maier and Kelley (1932)</td>
<td>( b \ a \ c )</td>
</tr>
<tr>
<td>Haas and Fisher (1976)</td>
<td>( f \ b \ a \ g \ c )</td>
</tr>
<tr>
<td>Berman and Brown (1983)</td>
<td>( a \ g \leq 0 \ c \leq 0 )</td>
</tr>
<tr>
<td>Berman and Brown (this paper)</td>
<td>( k_0 \ k_1 \leq 0 \ k_2 \leq 0 )</td>
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incorporated in the estimated heat capacity data points. In this paper we propose a revised heat capacity equation that provides a general technique for the extrapolation of the heat capacity of minerals to high temperature.

High temperature $C_p$ extrapolation

Theoretical constraints

The heat capacity of solids arises from vibration of atoms in a three dimensional lattice. Einstein (1907) and Debye (1912) derived equations for the temperature dependence of $C_p$, the heat capacity at constant volume, based on the assumption that atoms behave as harmonic oscillators at points within a crystal lattice. Although only the Debye equation leads to the $T^3$ relationship observed at low temperatures for non-conducting solids, both equations predict that $C_p$ approaches $3R/\text{afu}$ ($R$ is the gas constant, $\text{afu}$ = atoms/formula unit) at high temperatures. This so-called "limit of Petit and Dulong" (1819), which was initially based on their measurements of the heat capacity of solid elements, can also be derived from classical kinetic theory (Boltzmann 1871).

The heat capacity at constant pressure, $C_p$, is related to $C_v$ by

$$ C_p = C_v + \alpha^2 V T/\beta $$

where $\alpha$ is the coefficient of thermal expansion, $\beta$ is the coefficient of compressibility, $T$ is the absolute temperature, and $V$ is the volume. Thus, at high temperature, $C_p$ approaches the limit given by

$$ C_p = 3R + (\alpha^2 V T/\beta) T $$

Although anharmonicity and electronic contributions can lead to small departures from the $3R$ limit, the main difficulty in use of equation 2 stems from uncertainties in the variation of $\alpha$ and $\beta$ with temperature. The limited data available (e.g. the data of Raz (1983) for quartz, and of Sumino et al. (1983) for periclide) suggest however that $\alpha$ and $\beta$ vary sympathetically, and that the quantity $\alpha/\beta$ can be considered constant above the Debye temperature. Precise thermal expansion data for the aluminosilicates (Winter and Ghose 1979) indicate that the values of $(\partial^2 V/\partial T^2)$ are constant up to 1,600 K, which implies that thermal expansivities $(z = 1/V \partial^2 V/\partial T^2)$ may decrease with increasing temperature. Alternately, high temperature volumetric data for most minerals can be accurately fit by

$$ V = V_{298} e^{(z - T_s) + b/2 (T^2 - T_s^2)} $$

which results from the assumption that

$$ z = a + b T $$

Substitution of equation 4 into equation 2 yields

$$ C_p = 3R + (\alpha/\beta Va) T + (\alpha/\beta Vb) T^2 $$

For 16 minerals for which high temperature and pressure volumetric measurements are available, heat capacity has been calculated at 3,000 K (arbitrarily chosen as an upper temperature limit for most geologic applications) with equations 2 (assuming constant $\alpha$'s, evaluated at the highest temperatures at which data are available) and 5. On an atomic basis, the results are quite uniform (Table 2, columns 1 and 2), with the average heat capacity at 3,000 K for these minerals between $26.8 \pm 0.8$ and $29.3 \pm 1.9$ J/(afu.K). The differences between the two sets of values indicate that uncertainties in the temperature dependence of $\alpha$ and $\beta$ lead to uncertainties of approximately 10% in high temperature heat capacity.

Calculations with Empirical Equations

Extrapolations with the Haas-Fisher (HF) and Maier-Kelley (MK) equations are not in accord with these calculations, but it should be remembered that these equations were not developed as extrapolative tools, and potential users of the HF equation have been repeatedly cautioned against such use of this equation. We reemphasize this warning by tabulating high temperature $C_p$ values for several minerals calculated with both the MK and HF equations. Without additional constraints such as discussed by Lane and Ganguly (1980) and Holland (1981), the HF equation is not suited to the purpose of extrapolation (Table 2, column 5) because the use of five terms, unconstrained in sign, often produces inflections or maxima in the $C_p$ curve outside the range of the data. The MK equation leads to unreasonably high values for heat capacities at elevated temperatures (Table 2, column 4) because of the increasing contribution at high temperatures of the $bT^2$ term, although, for some phases with anomalously low high temperature heat capacity (e.g. quartz, pyrope), the MK extrapolations may appear to be in accord with the average theoretically derived high temperature heat capacities.

Heat capacity calculated from empirical equations can be constrained to approach a high temperature limit by