Thermodynamic functions at zero pressure and their relation to equations of state of minerals

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ABSTRACT

A simple numerical model for simultaneous optimization of heat capacity at constant pressure, \( C_P \), heat capacity at constant volume, \( C_V \), volume, \( V \), thermal expansion coefficient, \( \alpha \), isothermal, \( K_T \), and adiabatic, \( K_S \), bulk moduli at zero pressure, and \( PVT \) data for minerals has been developed. The basic function is the Debye energy, expressed through the Nernst-Lindemann energy function for \( T > 0.2\Theta \). Three additional empirical parameters are included in the expression for energy, which take into account anharmonicity, premelting, and other effects for real minerals. The volume vs. energy dependence is calculated on the basis of either the Wachtman et al. (1962) or the Suzuki (1975) model or their linear combination. Volume, \( V_{298} \), Nernst-Lindemann characteristic temperature, \( \Theta \), isothermal bulk modulus, \( K_{T298} \), its pressure derivative, \( K' \), Grüneisen parameter, \( \gamma \), isothermal Anderson-Grüneisen parameter, \( \delta_T \), and three empirical parameters, \( a, b, c \), which can be equal to zero for Debye-like solids, are fitting parameters of the model. The proposed model enables one to calculate thermodynamic functions of simple substances, oxides, and minerals over a temperature range from \( 0.2\Theta \) up to the melting temperature with a deviation within the scatter of experimental data. Correlation of the proposed model with \( PVT \) data is considered. It is shown that the isothermal equation of state results in an unsatisfactory extrapolation of volume in extreme regions. The Wachtman et al. (1962) and the Suzuki (1975) models of the volume vs. energy are extended to high pressure. The high-pressure Wachtman et al. (1962) and Suzuki (1975) models are versions of the Mie-Grüneisen equation of state and allow temperature dependencies of thermodynamic functions for any isobar to be easily calculated. The model described here and the classical Mie-Grüneisen model are found to be equivalent at \( q = 1 \). The model is tested using rock salt, corundum, and lawsonite.

INTRODUCTION

Knowledge of thermodynamic functions of minerals and their internal consistency is the main requirement for computer modeling of chemical equilibria in Earth’s lower crust and upper mantle. During the last three decades, a series of internally consistent thermodynamic databases for minerals has been developed (e.g., Helgeson et al. 1978; Dorogokupets and Karpov 1984; Saxena and Chatterjee 1986; Berman 1988; Gotschalk 1997; Holland and Powell 1998; Chatterjee et al. 1998). These databases are intended for studying mineral equilibria at moderate temperature and pressure. In these databases, the enthalpy and entropy of minerals, or enthalpy only, are optimized. Heat capacity is, as a rule, either not optimized or is optimized separately and is included in databases as an independent function. Furthermore, the simple equations of state used in these databases and the parameters defining dependence of volume on temperature and pressure are usually accepted as they are given in the literature and, with rare exceptions, are not discussed. These assumptions are quite justified under moderate temperatures and pressures, when the influence of errors connected with volume is insignificant in comparison with errors in enthalpy, entropy, and heat capacity equations. Databases directed toward computing mineral equilibria in the planet’s mantle are also available (e.g., Fei and Saxena 1986; Fabrichnaya and Kuskov 1994; Saxena et al. 1993; Kuskov 1995; Pankov et al. 1996). In these compilations attention is primarily given to optimization of thermodynamic parameters that define the dependence of volume on temperature and pressure. Hence, we see that a correct and internally consistent temperature dependence of heat capacity, thermal expansion coefficient, and bulk modulus are important for databases. Nevertheless, experimental data on these functions can be ambiguous even for key minerals and substances. Various sets of experimental data can differ by several per cent for heat capacity up to tens of per cent for the thermal expansion coefficient. Some combination of parameters from various sets of experimental data can yield quite different values, and the choice of the best one is arbitrary. One example is the product \( \alpha K_T \), where \( \alpha \) is the volume thermal expansion coefficient and \( K_T \) is the isothermal bulk modulus (Anderson 1996).

In the literature, substantial attention is given to the analytical description of heat capacity and thermal expansion coefficient by separate equations. A review of this work can be