American Mineralogist, Volume 85, pages 329–337, 2000

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, α, 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, Θ, isothermal bulk modulus, K_{T298}, its pressure derivative, K', Grüneisen parameter, γ, isothermal Anderson-Grüneisen parameter, δ_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 0.2Θ 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 $q \approx 1$. The model is tested using rock salt, corundum, and lawsonite.