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Research paper

# Microsoft excel spreadsheets for calculation of $P$ – $V$ – $T$ relations and thermodynamic properties from equations of state of MgO, diamond and nine metals as pressure markers in high-pressure and high-temperature experiments

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## ABSTRACT

We present Microsoft Excel spreadsheets for calculation of thermodynamic functions and  $P$ – $V$ – $T$  properties of MgO, diamond and 9 metals, Al, Cu, Ag, Au, Pt, Nb, Ta, Mo, and W, depending on temperature and volume or temperature and pressure. The spreadsheets include the most common pressure markers used in *in situ* experiments with diamond anvil cell and multianvil techniques. The calculations are based on the equation of state formalism via the Helmholtz free energy. The program was developed using Visual Basic for Applications in Microsoft Excel and is a time-efficient tool to evaluate volume, pressure and other thermodynamic functions using  $T$ – $P$  and  $T$ – $V$  data only as input parameters. This application is aimed to solve practical issues of high pressure experiments in geosciences and mineral physics.

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## 1. Introduction

Recently a significant progress has been achieved in the study of  $P$ – $V$ – $T$  properties of minerals and other materials in relation to the Earth and planetary mantle and core (Bassett, 2009; Hemley and Percy, 2010; Dubrovinsky et al., 2015). The major experimental techniques are diamond anvil cells and multianvil apparatus. One of the most important issues of those studies is correct measurement of pressure. However, there are no efficient barometers at pressures higher 100–300 GPa. The pressure in diamond anvil cells is typically calibrated using reference scales. Those scales are based on the equations of state of materials with a known pressure versus volume and temperature. The most popular pressure markers are MgO, Au, W, Pt, etc.

We have already published several equations of state, which can be used to estimate pressure (Dorogokupets and Oganov, 2003, 2006, 2007; Dorogokupets and Dewaele, 2007; Dorogokupets, 2010; Dorogokupets et al., 2012, 2015; Sokolova et al., 2013; Litasov et al., 2013a, b). Previously we have reported tabulated thermodynamic

functions calculated in respect to  $T$ – $P$  or  $T$ – $V$  for most of them (Dorogokupets, 2002, 2007; Dorogokupets et al., 2015; Litasov et al., 2013c, d). However, they are not convenient to practical use if a user cannot follow the complex thermodynamic formalism as presented in the original papers. In this paper we present MS Excel spreadsheets for simple and operational calculations of the unit cell volume, pressure and other thermodynamic properties of MgO, diamond and 9 metals, Al, Cu, Ag, Au, Pt, Nb, Ta, Mo, and W, at pressures and temperatures exceeding 400 GPa and 3000 K.

## 2. Thermodynamic model

## 2.1. Pressure calculation

The pressure is calculated from equation:

$$P_{\text{real}} = P_{298} + P_{\text{th}}, \quad (1)$$

where  $P_{298}$  is pressure at reference isotherm  $T_0$  or a potential part of the pressure, which depends only on volume, and  $P_{\text{th}}$  is the thermal part of real pressure, which depends on volume and temperature.

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Pressure at the reference isotherm of 298.15 K is determined from the Holzapfel equation (Holzapfel, 2001):

$$P_{298}(V) = 3K_0X^{-5}(1 - X)\exp[c_0(1 - X)](1 + c_2X(1 - X)), \quad (2)$$

where  $X = (V/V_0)^{1/3}$ ,  $c_0 = -\ln(3K_0/P_{FCO})$ ,  $P_{FCO} = 1003.6(nZ/V_0)^{5/3}$ ,  $c_2 = 1.5(K' - 3) - c_0$ ,  $V$  is volume,  $V_0$  is volume under standard conditions ( $T = 298.15$  K,  $P = 1$  bar),  $n$  is number of atoms in a chemical formula,  $K_0 = -V(\partial P_{298}/\partial V)_T$  is the isothermal bulk modulus under standard conditions,  $K' = \partial K_0/\partial P_{298}$ , and  $Z$  is atomic number.

The atomic number of elements in compounds (for MgO) is described by the following expression (Knopoff, 1965):

$$Z^{2/3} = \frac{\sum n_i Z_i^{5/3}}{\sum n_i Z_i}, \quad (3)$$

where  $n_i$  is number of atoms  $i$  with atomic number  $Z_i$  in a formula unit.

Eq. (2) is used because as interpolation between the low and high pressure points according to the Thomas–Fermi model at an infinite compression, when  $x \rightarrow 0$  ( $x = V/V_0$  is compression).

Differentiating Eq. (2) with respect to volume yields a potential part of the isothermal bulk modulus and its pressure derivative at the reference isotherm, which depends on volume only:

$$K_{T_0} = -V \left( \frac{\partial P_{298}}{\partial V} \right)_T = K_0 X^{-5} \exp[c_0(1 - X)] \left[ \begin{aligned} &(5 - 4X)(1 + c_2X(1 - X)) + \\ &+ c_0X(1 - X)(1 + c_2X(1 - X)) - \\ &- (1 - X)(c_2X - 2c_2X^2) \end{aligned} \right] \quad (4)$$

$$K' = \left( \frac{\partial K_{T_0}}{\partial P_{298}} \right)_T = \frac{1}{3} X \left[ c_0 + \frac{5}{X} + \frac{(2X - 1)(c_0 + 4c_2) - 2(3c_2X^2 + 2c_2X + 2)}{(1 + c_2X(1 - X))(5 - 4X + c_0X - c_0X^2) - c_2X(1 - X)^2} \right] \quad (5)$$

The thermal part of a real pressure is expressed as:

$$P_{th} = - \left( \frac{\partial F_{th}}{\partial V} \right)_T, \quad (6)$$

where  $F_{th}$  is the thermal part of Helmholtz free energy depending on volume and temperature.

As has been shown earlier (Dorogokupets and Dewaele, 2007; Dorogokupets, 2010), the thermodynamic functions at  $T > 298.15$  K can be calculated using the Debye or Einstein model or their combination. We use the Einstein model and express the thermal part of the Helmholtz free energy as a sum of Einstein temperature contribution and the contribution of free electrons accounted for by classical equation (Zharkov and Kalinin, 1971):

$$F_{th}(V, T) = m_i RT \ln \left( 1 - \exp \frac{-\Theta_i}{T} \right) + \left( -\frac{3}{2} n \text{Re}_0 x^g T^2 \right), \quad (7)$$

where  $m_i$  is the Einstein member ( $i=1, 2$ ),  $m_1 + m_2 = 3n$ ,  $n$  is number of atoms in a chemical formula of compound,  $\Theta_i$  is the Einstein characteristic temperature, which depends on volume and temperature ( $\Theta_{\text{Einstein}} \approx 0.775 \Theta_{\text{Debye}}$ ),  $e_0$  is a free electrons parameter,  $g$  is an electronic analogue of the Grüneisen parameter,  $x = V/V_0$ , and  $R$  the gas constant ( $8.31446 \text{ JK}^{-1} \text{ mol}^{-1}$ ).

We use two Einstein temperature contributions in Eq. (7) because it provide more accurately approximation of heat capacities of minerals in a range from 100 K to the melting temperature. Then Eq. (7) can be expressed as:

$$F_{th}(V, T) = m_1 RT \ln \left( 1 - \exp \frac{-\Theta_1}{T} \right) + m_2 RT \ln \left( 1 - \exp \frac{-\Theta_2}{T} \right) - \frac{3}{2} n \text{Re}_0 x^g T^2, \quad (8)$$

where characteristic temperatures  $\Theta_1$  and  $\Theta_2$  can be expressed as (Dorogokupets and Oganov, 2004):

$$\Theta_i = \Theta(V)_i \exp \left( \frac{1}{2} aT \right) = \Theta(V)_i \exp \left( \frac{1}{2} a_0 x^m T \right). \quad (9)$$

Here,  $\Theta(V)_i$  is volume dependence of characteristic temperature ( $i=1, 2$ ),  $a_0$  is an intrinsic anharmonicity parameter and  $m$  is an anharmonic analogue of the Grüneisen parameter.

The volume dependence of characteristic temperature in Eq. (9) is described by the following equation:

$$\Theta(V)_i = \Theta_{0i} x^{1/6 - \delta} K_0^{-1/2} (K_{T_0} - 2tP_{298}/3)^{1/2}, \quad (10)$$

where  $\Theta_{0i}$  is characteristic temperature under standard conditions ( $i=1, 2$ ),  $K_0$ ,  $K_{T_0}$  and  $P_{298}$  are considered at the reference isotherm,  $t$  can be equal to 0, 1 and 2, which corresponds to the Slater, Dugdale–MacDonald, and Zubarev–Vashchenko models, respectively, and  $\delta$  is an additive normalizing constant.

Eq. (10) is obtained by integration the volume dependence of the Grüneisen parameter, which is expressed as (Zharkov and Kalinin, 1971; Burakovsky and Preston, 2004):

$$\gamma = \frac{\frac{K'}{2} - \frac{1}{6} - \frac{t}{3} \left( 1 - \frac{P_{298}}{3K_{T_0}} \right)}{1 - \frac{2tP_{298}}{3K_{T_0}}} + \delta. \quad (11)$$

Note that in our previous works (Dorogokupets et al., 2012; Sokolova et al., 2013) Eqs. (10 and 11) contained typos. Here we present corrected equations. The volume dependence of the Grüneisen parameter can be calculated using different equations. This issue has been discussed by many authors (Al'tshuler et al., 1987; Taravillo et al., 1996; Stacey and Davis, 2004; Shanker et al., 2007; Srivastava and Sinha, 2009). Eq. (11) is used because it is based on the Thomas–Fermi model and gives a correct limit of the Grüneisen parameter ( $\gamma \rightarrow 0.5$ ) for solids at a very high compression up to  $x=0.6$ . The compression of 0.6 covers the experimental pressures in the reference studies, which exceed 400 GPa.

Differentiation of Eq. (7) with respect to volume at constant temperature allows calculation of the thermal part of real pressure:

$$P_{th} = - \left( \frac{\partial F_{th}}{\partial V} \right)_T = 3nR \frac{\left( \gamma - \frac{m}{2} a_0 x^m T \right)}{V} \left[ \frac{\Theta_i}{\exp(\Theta_i/T) - 1} \right] + \frac{3}{2} n \text{Re}_0 x^g T^2 \frac{g}{V}. \quad (12)$$

Similar differentiation of Eq. (12) allows calculation of the thermal part of isothermal bulk modulus:

$$K_{Tth} = -V \left( \frac{\partial P_{th}}{\partial V} \right)_T = -3nR \left[ \begin{aligned} &\frac{\Theta_i}{\exp(\Theta_i/T) - 1} \frac{q\gamma - \gamma}{V} - \\ &- \frac{\gamma \Theta_i}{V(\exp(\Theta_i/T) - 1)} \left( \gamma - \frac{m}{2} a_0 x^m T \right) + \\ &+ \frac{\gamma \Theta_i^2 \exp(\Theta_i/T)}{VT(\exp(\Theta_i/T) - 1)^2} \left( \gamma - \frac{m}{2} a_0 x^m T \right) + \\ &+ \frac{m}{2} a_0 x^m T \frac{\Theta_i}{V(\exp(\Theta_i/T) - 1)} \left( \gamma - \frac{m}{2} a_0 x^m T \right) - \\ &- \frac{m}{2} a_0 x^m \frac{\Theta_i^2 \exp(\Theta_i/T)}{V(\exp(\Theta_i/T) - 1)^2} \left( \gamma - \frac{m}{2} a_0 x^m T \right) - \\ &- \frac{m}{2} a_0 x^m T \frac{\Theta_i(m-1)}{V(\exp(\Theta_i/T) - 1)} - \\ &- \frac{1}{2} e_0 x^g T^2 (1 - g) \frac{g}{V} \end{aligned} \right] \quad (13)$$

where  $q = (\partial \ln \gamma / \partial \ln V)_T$  as calculated by numerical differentiation.

Differentiating Eq. (12) with respect to temperature at constant volume obtains the pressure slope  $(\partial P_{th} / \partial T)_V$  as:

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