# Thermodynamic Functions and Properties of MgO at High Compression and High Temperature

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The complete thermodynamic functions for MgO are presented for the temperature range 300–2000 K and the pressure range 0–150 GPa, both as tables and as graphs. Careful attention is given to the temperature and pressure dependence of the coefficient of thermal expansion $\alpha$ and the isothermal bulk modulus $K_T$, which are the major corrections to the thermodynamic functions in extreme conditions. Our equations efficiently use the fact that the product $\alpha K_T$ varies only slightly with either temperature or with volume, although scrupulous care is taken to account for the actual numbers. The corrections are now possible due to recent measurements of the bulk modulus up to 1800 K. The Birch Murnaghan equation of state is used to account for certain terms in the expressions for internal energy and enthalpy. The parameters used in the Birch–Murnaghan equation of state are given as functions of temperature. The parameters which presently limit the calculations of thermodynamic functions to even higher temperatures and pressures and limit the applications of this method to other minerals are: (1) the uncertainty of the thermal expansivity at temperatures above 1500 K, and (2) the uncertainty of the temperature dependence of $(\partial K_T/\partial T)_P$ at temperatures above 800 K.

Key words: thermodynamic functions; high-temperature properties; mineral physics; entropy of MgO; Gibbs energy of MgO; Helmholtz energy of MgO.

## Contents

## 1. Introduction

The principal objective of this work is to evalute and publish the data for all the thermodynamic functions of an important mineral, MgO or periclase, with a temperature range of 300 to 2000 K, and with a compression range of $V/V_0 = 1$ to $V/V_0 - 0.7$ (corresponding to $P \approx 150$ GPa).

It is well known that the computations of thermodynamic functions (entropy, for example) require knowledge of the thermal expansivity $\alpha$ and compressibility $\kappa$ as well as the specific heat. The pressure (or volume) and temperature variation of $\alpha$ and $\kappa$ contribute to the pressure (or volume) and temperature variation of the thermodynamic functions. The tabulation of these thermodynamic functions in the extreme ranges of temperature and pressure requires a good understanding of the equation of state, elasticity at very high temperature, anharmonicity of the solid, and the thermal expansivity at high temperature.

Recent experimental progress in the thermal equation of state has clarified the volume and high-temperature corrections to the thermal pressure, $P_{TH}$ and to the isothermal bulk modulus $K_T$ (the reciprocal of the compressibility $\kappa$), for MgO.[1] This progress is represented by the ability to measure elastic constants at high temperatures (in fact as high as 1825 K) using new resonance measurement techniques.[2,3]

It has become apparent from this recent research that it is best to treat $\alpha K_T$ as a single parameter, since the product varies little with volume or temperature, whereas both $\alpha$ and $K_T$ each vary significantly with volume and with temperature. The physical significance of the single parameter $\alpha K_T$ is that it is identical to the important function $(\partial P/\partial T)_v$.

A preliminary publication on a few graphs of the thermodynamic functions as well as the complete derivation of the basic equations have been presented elsewhere.[4] The graphs and tables presented here are a complete set, and are based upon published data.[5-7]

The molecular weight of MgO is taken to be 40.3114, and the conversion between calories and joules is taken to be 4.1855 J/cal.[8] We make much use of the conversion between pressure and energy density: 1 GPa = $10^3$ J/ml.

The important input thermodynamic data on MgO are given in Table 1: The adiabatic bulk modulus $K_S$ is taken from the experiments of Sumino et al.[5] with the values at

higher $T$ coming from Isaak et al.[9]; the data on the coefficient of thermal expansion $\alpha$ are from Suzuki et al.[6]; and the data on specific heat, $C_P$ are from the "CODATA" thermodynamic tables of Garvin et al.[7] Table 1 gives $\alpha$, the density $\rho$, $K_S$, and $C_P$, all at constant pressure $P = 0$, and as functions of $T$ up to 2000 K. In this table, we also present the value of the Grüneisen parameter, $\gamma$ vs $T$ at constant $P = 0$ computed from $\gamma = \alpha K_S/(\rho C_P)$, and the resultant specific heat versus $T$ at constant $V$, $C_V$, computed from $C_P/C_V = 1 + \alpha \gamma T$. Table 1 constitutes the basic thermodynamic data. From these data we list in Table 2 the following calculated fundamental thermodynamic parameters versus $T$ at $P = 0$: the isothermal bulk modulus $K_T$ where $K_S/K_T = 1 + \alpha \gamma T$; $\alpha K_T$; $(\partial K_T/\partial T)_P$; the computed isochoric temperature derivative of $K_T$, $(\partial K_T/\partial T)_V$; and the thermal pressure $P_{TH}$ where

$$P_{TH}(T) - P_{TH}(T_0) = \int_{T_0}^{T} \alpha K_T \, dT.$$

The equation relating $(\partial K_T/\partial T)_V$ to input parameters is shown in the Appendix [Eqs. (A4) and (A5) and discussion following Eq. (18)].

## 2. Thermodynamic Functions of MgO

### 2.1. Entropy Versus Volume and Temperature

The change of entropy with volume from $V_0$ to $V$, or $\chi = V/V_0$ from 1 to $V/V_0$, along an isotherm $T^*$ is given by (see Appendix, Sec. 6.1.)

$$S(T^*,\chi) - S(T^*,1)$$
$$= -(\alpha K_T)_{T^*} V_0 \left(1 - \frac{V}{V_0}\right)$$
$$+ wV_0 \left(\frac{V}{V_0} \ln \frac{V_0}{V} + \frac{V}{V_0} - 1\right)$$
$$= -(\alpha K_T)_{T^*} \left(\frac{1}{\rho_0}\right)(1 - \chi)$$
$$+ w\left(\frac{1}{\rho_0}\right)\left(\chi \ln \frac{1}{\chi} + \chi - 1\right), \quad (1)$$

where $\rho_0$ = zero pressure density at $T^*$. The reference volume $V_0$ is taken at $P = 0$ and $T = 300$ K. The parameter

$$w = (\partial K_T/\partial T)_V \quad (2)$$

Table 1. Laboratory input data

| $T$ (K) | $\rho$ (g/ml) | $\alpha$ ($10^{-6}$ K$^{-1}$) | $K_S$ (GPa) | $C_P$ (J g$^{-1}$ K$^{-1}$) | $C_V$ (J g$^{-1}$ K$^{-1}$) | $\gamma$ |
|---|---|---|---|---|---|---|
| 300 | 3.585 | 31.2 | 163.9 | 0.928 | 0.915 | 1.54 |
| 350 | 3.579 | 33.9 | 163.1 | 1.006 | 0.988 | 1.54 |
| 400 | 3.573 | 35.7 | 162.3 | 1.061 | 1.038 | 1.53 |
| 450 | 3.566 | 37.2 | 161.5 | 1.100 | 1.073 | 1.53 |
| 500 | 3.559 | 38.4 | 160.7 | 1.130 | 1.098 | 1.53 |
| 550 | 3.552 | 39.3 | 159.9 | 1.154 | 1.117 | 1.53 |
| 600 | 3.545 | 40.2 | 158.9 | 1.173 | 1.132 | 1.54 |
| 650 | 3.538 | 40.8 | 157.9 | 1.190 | 1.143 | 1.53 |
| 700 | 3.531 | 41.4 | 157.1 | 1.204 | 1.153 | 1.53 |
| 750 | 3.524 | 42.0 | 156.0 | 1.216 | 1.160 | 1.53 |
| 800 | 3.516 | 42.6 | 155.1 | 1.227 | 1.166 | 1.53 |
| 850 | 3.509 | 43.2 | 154.1 | 1.237 | 1.171 | 1.53 |
| 900 | 3.501 | 43.8 | 153.1 | 1.246 | 1.175 | 1.54 |
| 950 | 3.494 | 44.1 | 152.1 | 1.254 | 1.179 | 1.53 |
| 1000 | 3.486 | 44.7 | 151.1 | 1.262 | 1.181 | 1.54 |
| 1050 | 3.478 | 45.0 | 150.0 | 1.269 | 1.184 | 1.53 |
| 1100 | 3.470 | 45.6 | 148.9 | 1.276 | 1.185 | 1.53 |
| 1150 | 3.462 | 45.9 | 147.7 | 1.282 | 1.187 | 1.53 |
| 1200 | 3.454 | 46.5 | 146.7 | 1.289 | 1.187 | 1.53 |
| 1250 | 3.446 | 46.8 | 145.6 | 1.295 | 1.189 | 1.53 |
| 1300 | 3.438 | 47.1 | 144.4 | 1.301 | 1.190 | 1.52 |
| 1350 | 3.430 | 47.7 | 143.2 | 1.306 | 1.190 | 1.53 |
| 1400 | 3.422 | 48.0 | 142.0 | 1.312 | 1.191 | 1.52 |
| 1450 | 3.413 | 48.6 | 140.8 | 1.318 | 1.190 | 1.52 |
| 1500 | 3.405 | 48.9 | 139.7 | 1.323 | 1.191 | 1.52 |
| 1550 | 3.397 | 49.2 | 138.4 | 1.329 | 1.192 | 1.51 |
| 1600 | 3.388 | 49.8 | 137.3 | 1.334 | 1.191 | 1.51 |
| 1650 | 3.380 | 50.1 | 136.2 | 1.340 | 1.192 | 1.51 |
| 1700 | 3.371 | 50.4 | 134.9 | 1.346 | 1.193 | 1.50 |
| 1750 | 3.363 | 51.0 | 133.8 | 1.352 | 1.192 | 1.50 |
| 1800 | 3.354 | 51.3 | 132.7 | 1.358 | 1.193 | 1.50 |
| 1850 | 3.346 | 51.9 | 131.7 | 1.364 | 1.192 | 1.50 |
| 1900 | 3.337 | 52.2 | 130.7 | 1.370 | 1.194 | 1.49 |
| 1950 | 3.328 | 52.8 | 129.7 | 1.377 | 1.193 | 1.49 |
| 2000 | 3.319 | 53.3 | 128.7 | 1.384 | 1.194 | 1.49 |

The density, $\rho$, is calculated from the volume thermal expansivity, $\alpha$. It is taken from Suzuki et al.[6] The adiabatic bulk modulus, $K_S$, is taken from measurements and extrapolations of Sumino et al.,[5] confirmed and extended by Isaak et al.[9] The source of data on specific heat, $C_P$, is Garvin et al.[7] The Grüneisen ratio, $\gamma$, is calculated from other parameters by $\gamma = \alpha K_S V / C_P$. The specific heat, $C_V$, is calculated from $C_P$ and $\gamma$ according to Eq. (4).

is listed in Table 2. The parameter $(\alpha K_T)_{T*}$ designates the value of $\alpha K_T$ at the temperature of the selected isotherm $T*$ and at $P = 0$.

The second term on the right-hand side of Eq. (1), involving $w$, is small compared to the first, but becomes increasingly important at high compression. In some solids, for example NaCl, $w$ is vanishingly small and can be entirely neglected; but for MgO, $w$ has a measurable effect on entropy.

Units of $\alpha K_T / V_0 = \alpha K_T / \rho_0$ are J g$^{-1}$ K$^{-1}$. Units in Table 1 are $K_T$ in GPa, $\rho_0$ in g/ml, and the exponent of $\alpha$ is $10^{-6}$ (typical values: $K_T = 160$ GPa $= 1.60 \times 10^5$ J/ml; $\alpha = 31.2 \times 10^{-6}$ K$^{-1}$; $\rho_0 = 3.587$ g/ml, so $\alpha K_T / \rho_0 = 1.39$ J g$^{-1}$ K$^{-1}$; multiplying by $(40.3114/4.1855) = 9.6312$ gives the units of $\alpha K_T V_0$ in cal mol$^{-1}$ K$^{-1}$. (The value 4.1855 comes from Jerrard and McNeill.[8])

The variation of entropy at constant $V = V_0$, or $\chi = 1$, from $T_0$ to $T*$, is given by the standard formula

$$S_{\chi = 1}(T*) - S_{\chi = 1}(T_0) = \int_{T_0}^{T*} C_V \frac{dT}{T}, \qquad (3)$$

where

$$C_V = \frac{C_P}{1 + \alpha \gamma T}. \qquad (4)$$

Standard conditions are taken to be 300 K and $P = 1$ atmosphere. Thus, $T_0 = 300$ K. This means that at absolute zero, $\chi = 0.988$. The input data on entropy are at constant pressure, called here $S_P$, given by Garvin et al.[7]

The entropy of $S_{\chi = 1}$ at 300 K is found by using the tabled value of $S_P$ at 300 K and correcting by calculating

$$S_P(300) - S_{\chi = 1}(300) = \int_0^{300} (C_P - C_V) \frac{dT}{T}. \qquad (5)$$

Using the published data of $C_V - C_P$ given by Barron et al.,[10] we find the correction, Eq. (5), to be 0.00378 J g$^{-1}$ K$^{-1}$, so that $S_{\chi = 1}(300) = 0.6705$ J g$^{-1}$ K$^{-1}$, since $S_P(300) = 0.6742$ J g$^{-1}$ K$^{-1}$ (see Gavin et al.,[7] as listed in Table 3).

Using Eqs. (1) and (3), the entropy versus $T$ at constant $\chi$ was calculated and is listed in Table 3. Isochoric plots of $S_\chi$ vs $T$ are shown in Fig. 1. The entropy versus $\chi$ at constant $T$ is listed in Table 4.

## 2.2. Internal Energy Versus Volume and Temperature

The change of internal energy $U$ with volume, $V_0$ to $V$, or $\chi$ from 1 to $V/V_0$, along an isotherm $T*$ is given by

Table 2. Thermodynamic data calculated from Table 1

| $T$ (K) | $K_T$ (GPa) | $\alpha K_T$ (MPa/K) | $(\partial K_T / \partial T)_P$ (MPa/K) | $(\partial K_T / \partial T)_V$ (MPa/K) | $P_{TH}$ (GPa) |
|---|---|---|---|---|---|
| 300 | 162 | 5.04 | -27.7 | -8.0 | 0.717 |
| 350 | 160 | 5.43 | -27.5 | -6.3 | 0.98 |
| 400 | 159 | 5.67 | -27.3 | -5.2 | 1.26 |
| 450 | 157 | 5.86 | -27.3 | -4.5 | 1.55 |
| 500 | 156 | 6.00 | -28.2 | -4.8 | 1.84 |
| 550 | 155 | 6.08 | -28.7 | -5.1 | 2.15 |
| 600 | 153 | 6.16 | -28.7 | -4.7 | 2.45 |
| 650 | 152 | 6.19 | -29.0 | -4.9 | 2.76 |
| 700 | 150 | 6.23 | -29.0 | -4.7 | 3.07 |
| 750 | 149 | 6.25 | -29.6 | -5.3 | 3.38 |
| 800 | 147 | 6.28 | -30.4 | -6.0 | 3.70 |
| 850 | 146 | 6.30 | -29.9 | -5.4 | 4.01 |
| 900 | 144 | 6.32 | -30.1 | -5.5 | 4.33 |
| 950 | 143 | 6.30 | -30.0 | -5.5 | 4.64 |
| 1000 | 141 | 6.32 | -30.3 | -5.8 | 4.96 |
| 1050 | 140 | 6.29 | -31.0 | -6.6 | 5.27 |
| 1100 | 138 | 6.31 | -31.2 | -6.7 | 5.59 |
| 1150 | 137 | 6.28 | -31.2 | -6.8 | 5.90 |
| 1200 | 135 | 6.28 | -30.8 | -6.4 | 6.22 |
| 1250 | 134 | 6.25 | -31.3 | -7.0 | 6.53 |
| 1300 | 132 | 6.22 | -31.5 | -7.3 | 6.84 |
| 1350 | 130 | 6.22 | -32.3 | -8.1 | 7.15 |
| 1400 | 129 | 6.19 | -32.1 | -8.1 | 7.46 |
| 1450 | 127 | 6.18 | -31.5 | -7.5 | 7.77 |
| 1500 | 126 | 6.15 | -31.4 | -7.5 | 8.08 |
| 1550 | 124 | 6.11 | -30.7 | -6.9 | 8.39 |
| 1600 | 123 | 6.10 | -30.5 | -6.8 | 8.69 |
| 1650 | 121 | 6.07 | -30.5 | -6.9 | 9.00 |
| 1700 | 120 | 6.03 | -29.9 | -6.4 | 9.30 |
| 1750 | 118 | 6.02 | -29.7 | -6.3 | 9.60 |
| 1800 | 117 | 5.98 | -28.6 | -5.3 | 9.90 |
| 1850 | 115 | 5.98 | -27.9 | -4.6 | 10.20 |
| 1900 | 114 | 5.94 | -27.9 | -4.8 | 10.50 |
| 1950 | 112 | 5.94 | -27.6 | -4.6 | 10.79 |
| 2000 | 111 | 5.92 | -27.4 | -4.4 | 11.09 |

The isothermal bulk modulus, $K_T$, is calculated from $K_T = K_S/(1 + \alpha \gamma T)$. The parameter $\alpha K_T$ is calculated from the fields $\alpha$ and $K_T$. The derivative $(\partial K_T / \partial T)_P$, is calculated from the values in the fields $T$ and $K_T$ (at 10 degree intervals). The isochoric bulk modulus $(\partial K_T / \partial T)_V$ is calculated from Eq. (A6), where $K_T' = 4.17$ and is measured to be independent of temperature.[14] The thermal pressure, $P_{TH}$, is calculated from $P_{TH} = \int \alpha K_T dT$.

Table 3.  Entropy vs. T at constant $\chi$, $S(T,V/V_0)$

| T (K) | S(T,1.0) | S(T,0.95) | S(T,0.90) | S(T,0.85) (J g$^{-1}$ K$^{-1}$) | S(T,0.80) | S(T,0.75) | S(T,0.70) |
|---|---|---|---|---|---|---|---|
| 300 | 0.6705 | 0.60 | 0.53 | 0.46 | 0.39 | 0.33 | 0.26 |
| 350 | 0.817 | 0.74 | 0.66 | 0.59 | 0.51 | 0.43 | 0.35 |
| 400 | 0.953 | 0.87 | 0.79 | 0.72 | 0.64 | 0.56 | 0.48 |
| 450 | 1.077 | 1.00 | 0.91 | 0.83 | 0.75 | 0.67 | 0.59 |
| 500 | 1.192 | 1.11 | 1.02 | 0.94 | 0.86 | 0.78 | 0.69 |
| 550 | 1.297 | 1.21 | 1.13 | 1.04 | 0.96 | 0.87 | 0.79 |
| 600 | 1.395 | 1.31 | 1.22 | 1.14 | 1.05 | 0.97 | 0.88 |
| 650 | 1.486 | 1.40 | 1.31 | 1.23 | 1.14 | 1.05 | 0.97 |
| 700 | 1.571 | 1.48 | 1.40 | 1.31 | 1.22 | 1.13 | 1.05 |
| 750 | 1.651 | 1.56 | 1.47 | 1.39 | 1.30 | 1.21 | 1 13 |
| 800 | 1.736 | 1.64 | 1.55 | 1.46 | 1.37 | 1.29 | 1.20 |
| 850 | 1.797 | 1.71 | 1.62 | 1.53 | 1.44 | 1.35 | 1.27 |
| 900 | 1.864 | 1.77 | 1.68 | 1.59 | 1.51 | 1.42 | 1.33 |
| 950 | 1.928 | 1.84 | 1.75 | 1.66 | 1.57 | 1.48 | 1.39 |
| 1000 | 1.988 | 1.90 | 1.81 | 1.72 | 1.63 | 1.54 | 1 45 |
| 1050 | 2.046 | 1.96 | 1.87 | 1.78 | 1.69 | 1.60 | 1.51 |
| 1100 | 2.101 | 2.01 | 1.92 | 1.83 | 1.74 | 1.65 | 1.57 |
| 1150 | 2.154 | 2.06 | 1.97 | 1.88 | 1.80 | 1.71 | 1.62 |
| 1200 | 2.204 | 2.11 | 2.02 | 1.93 | 1.84 | 1.76 | 1.67 |
| 1250 | 2.254 | 2.16 | 2.07 | 1.98 | 1.90 | 1.81 | 1.72 |
| 1300 | 2.299 | 2.21 | 2.12 | 2.03 | 1.94 | 1.85 | 1.77 |
| 1350 | 2.344 | 2.25 | 2.16 | 2.07 | 1.99 | 1.90 | 1 81 |
| 1400 | 2.387 | 2.30 | 2.21 | 2.12 | 2.03 | 1.94 | 1.86 |
| 1450 | 2.429 | 2.34 | 2.25 | 2.16 | 2.07 | 1.98 | 1 90 |
| 1500 | 2.470 | 2.38 | 2.29 | 2.20 | 2.11 | 2.03 | 1 94 |
| 1550 | 2.509 | 2 42 | 2.33 | 2.24 | 2.15 | 2.07 | 1.98 |
| 1600 | 2.546 | 2.46 | 2.37 | 2.28 | 2.19 | 2.10 | 2 02 |
| 1650 | 2.583 | 2.49 | 2.40 | 2.32 | 2.23 | 2.14 | 2.05 |
| 1700 | 2.619 | 2.53 | 2.44 | 2.35 | 2.27 | 2 18 | 2.09 |
| 1750 | 2.653 | 2.56 | 2.48 | 2.39 | 2.30 | 2.21 | 2.13 |
| 1800 | 2.687 | 2.60 | 2.51 | 2.42 | 2.33 | 2.25 | 2 16 |
| 1850 | 2.720 | 2.63 | 2.54 | 2.45 | 2.37 | 2.28 | 2.19 |
| 1900 | 2.751 | 2.66 | 2.57 | 2.49 | 2.40 | 2 31 | 2 22 |
| 1950 | 2.782 | 2.69 | 2.60 | 2.52 | 2.43 | 2.34 | 2 25 |
| 2000 | 2.813 | 2.72 | 2.63 | 2.55 | 2.46 | 2 37 | 2 28 |

$$U(T^*,\chi) - U(T^*,1)$$
$$= (T^*\Delta S_\chi)_{T^*} - P_{TH}(1/\rho_0)(0.988 - \chi) - \int P_0\, dV,$$
$$(6)$$

(see Appendix). We see that the equation of state becomes important to $U$ through the term $\int P_0\, dV$. Here $\rho_0$ refers to the zero pressure value appropriate to the isotherm $T^*$. For $P_0$ (along the isotherm $T = 0$), we use the Birch–Murnaghan equation of state of the third degree.[11]

$$P_0 = P\left(\frac{\rho}{\rho_{00}}\right) = \frac{3}{2}K_0(y^{7/3} - y^{5/3})$$
$$\times \left[1 + \frac{3(K'_0 - 4)(y^{2/3} - 1)}{4}\right],$$
$$(7)$$

where $y = \rho/\rho_{00}$. $\rho_{00}$ is the absolute zero density at $P = 0$, so that for $\rho_{00}$ in Eq. (7) we have 3.6312 g/ml. In the integration of $P_0$, there arises a dimensionless expression multiplied by the term $K_0 V_{00}$, which is also $K_0/\rho_{00} = 166.2/3.6312$ GPa g$^{-1}$ ml$^{-1}$ = $4.577 \times 10^4$ J/g.
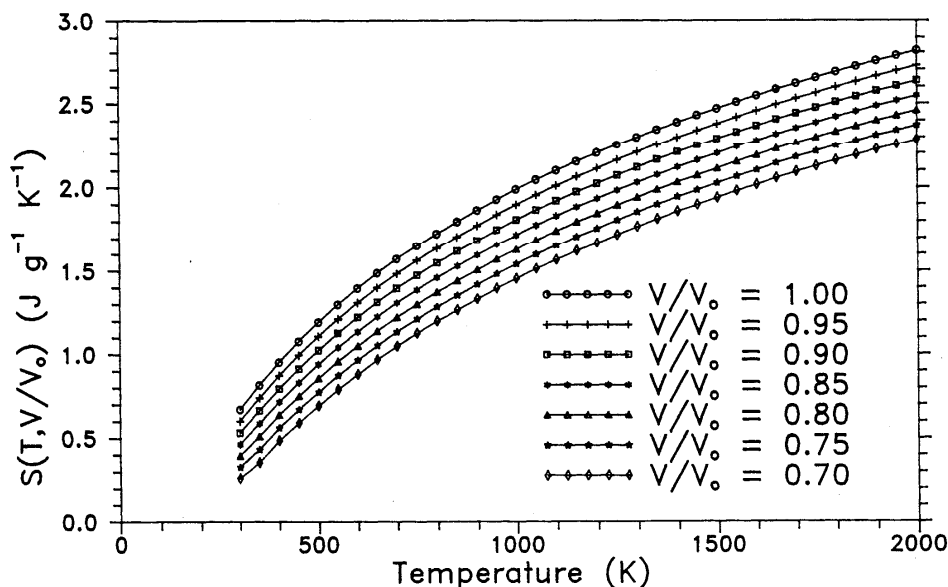


FIG 1  The isochoric plots of entropy, at constant $V/V_0$, vs $T$

Table 4.  Entropy vs. χ at constant T, $S(V/V_o)$

| χ=V/V$_o$ | S(χ,300) | S(χ,500) | S(χ,1000) | S(χ,1500) | S(χ,2000) |
|---|---|---|---|---|---|
| 0.70 | 0.260 | 0.69 | 1.45 | 1.94 | 2.28 |
| 0.72 | 0.286 | 0.73 | 1.49 | 1.97 | 2.32 |
| 0.74 | 0.313 | 0.76 | 1.52 | 2.01 | 2.35 |
| 0.76 | 0.340 | 0.79 | 1.56 | 2.04 | 2.39 |
| 0.78 | 0.367 | 0.82 | 1.59 | 2.08 | 2.42 |
| 0.80 | 0.394 | 0.86 | 1.63 | 2.11 | 2.46 |
| 0.82 | 0.421 | 0.89 | 1.66 | 2.15 | 2.49 |
| 0.84 | 0.449 | 0.92 | 1.70 | 2.18 | 2.53 |
| 0.86 | 0.476 | 0.96 | 1.74 | 2.22 | 2.56 |
| 0.88 | 0.503 | 0.99 | 1.77 | 2.25 | 2.60 |
| 0.90 | 0.531 | 1.02 | 1.81 | 2.29 | 2.63 |
| 0.92 | 0.559 | 1.06 | 1.84 | 2.33 | 2.67 |
| 0.94 | 0.587 | 1.09 | 1.88 | 2.36 | 2.71 |
| 0.96 | 0.614 | 1.12 | 1.92 | 2.40 | 2.74 |
| 0.98 | 0.642 | 1.16 | 1.95 | 2.43 | 2.78 |
| 1.00 | 0.6705 | 1.19 | 1.99 | 2.47 | 2.81 |
| 1.02 | 0.699 | 1.23 | 2.02 | 2.51 | 2.85 |
| 1.04 | 0.727 | 1.26 | 2.06 | 2.54 | 2.88 |
| 1.06 | 0.755 | 1.29 | 2.10 | 2.58 | 2.92 |
| 1.08 | 0.784 | 1.33 | 2.13 | 2.61 | 2.96 |
| 1.10 | 0.812 | 1.36 | 2.17 | 2.65 | 2.99 |
| 1.12 | 0.841 | 1.39 | 2.21 | 2.69 | 3.03 |
| 1.14 | 0.870 | 1.43 | 2.24 | 2.72 | 3.06 |
| 1.16 | 0.898 | 1.46 | 2.28 | 2.76 | 3.10 |
| 1.18 | 0.927 | 1.50 | 2.32 | 2.80 | 3.14 |

The variation of internal energy $U$ with temperature at $\chi = 1$ above $T = 300$ K is given by

$$U(T^*,1) - U(300,1) = \int_{300}^{T^*} C_V \, dT. \qquad (8)$$

We need the value of $U(300,1)$, which is obtained, for example, by integrating the values of $C_P - C_V$, as tabled by Barron et al.,[10] up to 300 K, or by computing the thermal pressure effect on the enthalpy (see Appendix, Sec. 6.4.). We find

$$U(300,\chi = 1) = 127.3 \text{ J/g for MgO.} \qquad (9)$$

One further explanation needs to be made for Eq. (7). This equation is in fact valid only at absolute zero. The value of $\rho_0$ for MgO at 0 K is 3.6312, compared with $\rho(300, P = 0) = 3.587$. In the calculations of the functions, we use $\rho_0 = 3.5877$ since our standard state is at 300 K. Properties at temperatures below 300° correspond to values of $\chi$ less than unity at $P = 0$ ($\chi = 0.988$ at $T = 0$).

Equations (6) and (7) were used to calculate $U$ vs $\chi$ and $T$, and the values are listed in Table 5 and plotted in Fig. 2.

## 2.3. The Helmholz Energy Versus Volume and Temperature

The Helmholz energy is given by

$$F = U - TS. \qquad (10)$$

Calculating $F$ is straightforward. The tabled results of $F$ vs $\chi$ at constant $T$ are given in Table 6. A plot of $F_\chi$ vs $T$ for MgO is shown in Fig. 3, and a plot of $F_T$ vs $\chi$ for MgO is shown in Fig. 4. Table 7 shows the Helmholtz energy versus $T$ at constant $\chi$.

The minimum of $F(T,V/V_0)$ locates the specific volume at $T$. We see from Fig. 4 that the minimum increases as $T$ increases, and this will obey the law $dV/V = \alpha dT$.

## 2.4. Entropy Versus Pressure and Temperature

The values of the constant pressure entropy, $S_P$ vs. $T$ at $P = 0$, $S_P(T,0)$ are taken from Garvin et al.,[7] and found in the first column of Table 8. The values of entropy versus $P$

Table 5.  Internal energy vs. T at constant χ, $U(T,V/V_o)$

| T (K) | U(T,1.0) | U(T,0.95) | U(T,0.90) | U(T,0.85) (J/g) | U(T,0.80) | U(T,0.75) | U(T,0 70) |
|---|---|---|---|---|---|---|---|
| 300 | 127.3 | 180 | 380 | 790 | 1440 | 2450 | 3910 |
| 350 | 175.0 | 240 | 440 | 840 | 1500 | 2490 | 3960 |
| 400 | 225.7 | 280 | 480 | 880 | 1540 | 2540 | 4000 |
| 450 | 278.5 | 330 | 530 | 930 | 1590 | 2590 | 4050 |
| 500 | 332.8 | 380 | 580 | 980 | 1640 | 2640 | 4110 |
| 550 | 388.3 | 440 | 640 | 1040 | 1700 | 2700 | 4170 |
| 600 | 444.5 | 490 | 690 | 1090 | 1750 | 2760 | 4230 |
| 650 | 501 4 | 550 | 750 | 1150 | 1810 | 2820 | 4290 |
| 700 | 558.8 | 610 | 810 | 1210 | 1870 | 2880 | 4360 |
| 750 | 616 6 | 660 | 860 | 1260 | 1930 | 2940 | 4420 |
| 800 | 674.7 | 720 | 920 | 1320 | 1990 | 3000 | 4490 |
| 850 | 733.1 | 780 | 980 | 1380 | 2050 | 3070 | 4550 |
| 900 | 791 8 | 840 | 1040 | 1440 | 2110 | 3130 | 4620 |
| 950 | 850.7 | 900 | 1100 | 1500 | 2170 | 3190 | 4690 |
| 1000 | 909.7 | 960 | 1160 | 1560 | 2230 | 3260 | 4750 |
| 1050 | 968.8 | 1020 | 1220 | 1620 | 2300 | 3330 | 4830 |
| 1100 | 1028 1 | 1070 | 1280 | 1690 | 2360 | 3390 | 4890 |
| 1150 | 1087.4 | 1130 | 1340 | 1750 | 2430 | 3460 | 4970 |
| 1200 | 1146.7 | 1190 | 1400 | 1810 | 2490 | 3520 | 5030 |
| 1250 | 1206 1 | 1250 | 1460 | 1870 | 2550 | 3590 | 5110 |
| 1300 | 1265.6 | 1310 | 1520 | 1930 | 2620 | 3660 | 5180 |
| 1350 | 1325.0 | 1370 | 1580 | 2000 | 2680 | 3730 | 5250 |
| 1400 | 1384.5 | 1430 | 1640 | 2060 | 2750 | 3800 | 5320 |
| 1450 | 1444.1 | 1490 | 1700 | 2120 | 2810 | 3860 | 5390 |
| 1500 | 1503.6 | 1550 | 1770 | 2180 | 2880 | 3930 | 5470 |
| 1550 | 1563.2 | 1620 | 1830 | 2250 | 2940 | 4000 | 5540 |
| 1600 | 1622.8 | 1670 | 1890 | 2310 | 3010 | 4070 | 5610 |
| 1650 | 1682.4 | 1740 | 1950 | 2370 | 3070 | 4140 | 5690 |
| 1700 | 1742 0 | 1800 | 2010 | 2440 | 3140 | 4210 | 5760 |
| 1750 | 1801.6 | 1860 | 2070 | 2500 | 3200 | 4270 | 5830 |
| 1800 | 1861.2 | 1920 | 2130 | 2560 | 3270 | 4340 | 5910 |
| 1850 | 1920.9 | 1980 | 2200 | 2620 | 3330 | 4410 | 5980 |
| 1900 | 1980.5 | 2040 | 2260 | 2690 | 3400 | 4480 | 6050 |
| 1950 | 2040 2 | 2100 | 2320 | 2750 | 3460 | 4550 | 6120 |
| 2000 | 2099 9 | 2160 | 2380 | 2810 | 3530 | 4620 | 6200 |

$V_o$ is standard volume at $T = 300$ K and $P = 1$ atmosphere.
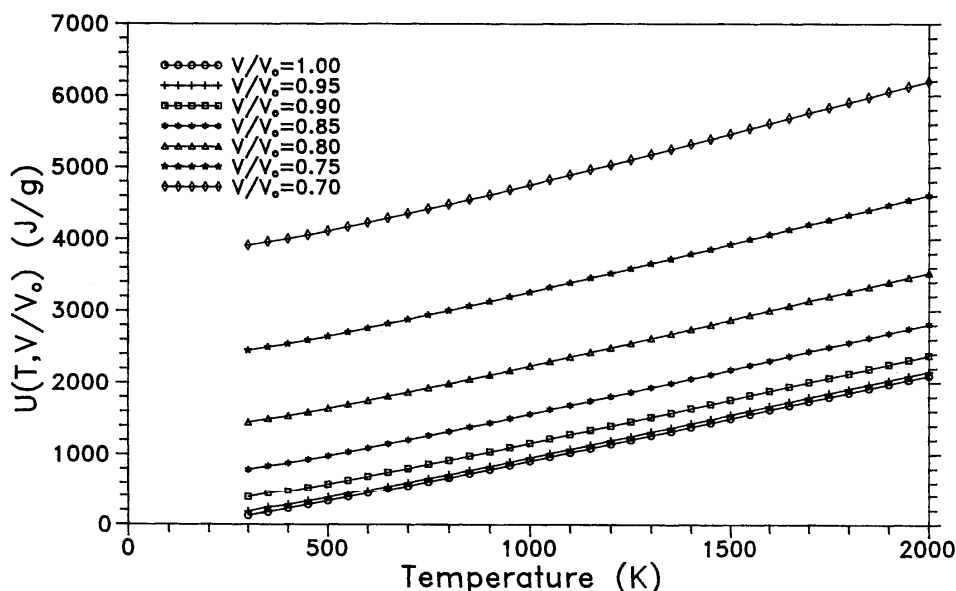
FIG. 2. The isochoric plots of internal energy $U_\gamma$ vs $T$.

along the isotherm $T^*$ are found to be (see Appendix)

$$S_P(T^*,P) - S_P(T^*,0) = -(\alpha K_T)_{T^*}(1/\rho_0)(1 - \chi_0)$$

$$- K_V(T^*,0)(1/\rho_0)$$

$$\times (\chi_0 \ln \chi_0 + 1 - \chi_0), \qquad (11)$$

where

$$\rho_0 = \rho(T^*,P = 0)$$

and

$$\chi_0 = \frac{V(T^*,P)}{V(T^*,P = 0)} . \qquad (12)$$

$V(T^*,P = 0)$ is found by integrating the coefficient of thermal expansivity:

Table 6. Helmholtz energy vs. $\chi$ at constant $T$, $F(V/V_o,T)$

| $\chi$-$V/V_o$ | $F(\chi,300)$ | $F(\chi,500)$ | $F(\chi,1000)$ (J/g) | $F(\chi,1500)$ | $F(\chi,2000)$ |
|---|---|---|---|---|---|
| 0.70 | 3830 | 3760 | 3300 | 2560 | 1630 |
| 0.72 | 3174 | 3100 | 2570 | 1820 | 860 |
| 0.74 | 2605 | 2520 | 1960 | 1180 | 180 |
| 0.76 | 2112 | 2020 | 1430 | 620 | -410 |
| 0.78 | 1689 | 1580 | 970 | 130 | -930 |
| 0.80 | 1330 | 1210 | 610 | -290 | -1390 |
| 0.82 | 1018 | 900 | 240 | -660 | -1780 |
| 0.84 | 759 | 630 | -50 | -980 | -2130 |
| 0.86 | 543 | 400 | -290 | -1250 | -2420 |
| 0.88 | 366 | 220 | -500 | -1480 | -2680 |
| 0.90 | 220 | 70 | -650 | -1670 | -2890 |
| 0.92 | 114 | -50 | -800 | -1830 | -3070 |
| 0.94 | 31 | -140 | -900 | -1960 | -3220 |
| 0.96 | -26 | -200 | -990 | -2060 | -3350 |
| 0.98 | -60 | -240 | -1040 | -2140 | -3450 |
| 1.00 | -74 | -260 | -1080 | -2200 | -3530 |
| 1.02 | -69 | -260 | -1100 | -2240 | -3580 |
| 1.04 | -47 | -250 | -1100 | -2260 | -3620 |
| 1.06 | -10 | -220 | -1080 | -2260 | -3640 |
| 1.08 | 40 | -170 | -1050 | -2260 | -3650 |
| 1.10 | 100 | -120 | -1000 | -2230 | -3650 |
| 1.12 | 170 | -50 | -950 | -2200 | -3630 |
| 1.14 | 260 | 30 | -890 | -2150 | -3600 |
| 1.16 | 350 | 120 | -820 | -2100 | -3570 |
| 1.18 | 450 | 210 | -730 | -2040 | -3520 |

$$V(T^*,P = 0) = \int_{T_0}^{T^*} \alpha \, dT + V(T_0,P = 0). \qquad (13)$$

To get $V(T^*,P)$ we must account for the opposite effects of pressure and temperature on the volume. The calculation is made by adding the decrease in $\Delta\chi$ due to pressure at absolute zero to the increase in $\Delta\chi$ due to $T$ at $P = 0$:

$$\Delta V(T^*,P) = \Delta V(T = 0,P) + \Delta V(T^*,P = 0), \qquad (14)$$

where, in general,

$$\Delta V = V_0(\chi - 1).$$

$\Delta V(0,P)$ as seen later in Table 13, is found by using the Birch–Murnaghan equation of state and $\Delta V(T^*,P = 0)$ is found from the values of $\rho$ in Table 1.

A listing of values for $S_P$ vs $T$ and $P$ as found in Table 8 is plotted in Fig. 5.

## 2.5. Enthalpy Versus Pressure and Temperature

The enthalpy versus $T$ at $P = 0$, $H(T,0)$, is copied from Garvin et al.[7] and shown as the first column in Table 9.

The variation of enthalpy versus pressure at constant temperature $T^*$ is found to be (see Appendix, Sec. 6.4.)

$$H(T^*,P) - H(T^*,0) = -\int_{V(T^*,0)}^{V(T^*,P)} K_T \, dV$$

$$+ T^*[S(T^*,P) - S(T^*,0)], \qquad (15)$$

where $K_T$ at $T = 0$ is found from the volume derivative of Eq. (7).

$$K_T(0,\chi) = K_{T_0}\left(\frac{y}{y_0}\right)^{5/3}$$

$$\times \left\{1 + \frac{1}{2}(3K'_0 - 5)\left[\left(\frac{y}{y_0}\right)^{2/3} - 1\right]\right\} . \qquad (16)$$
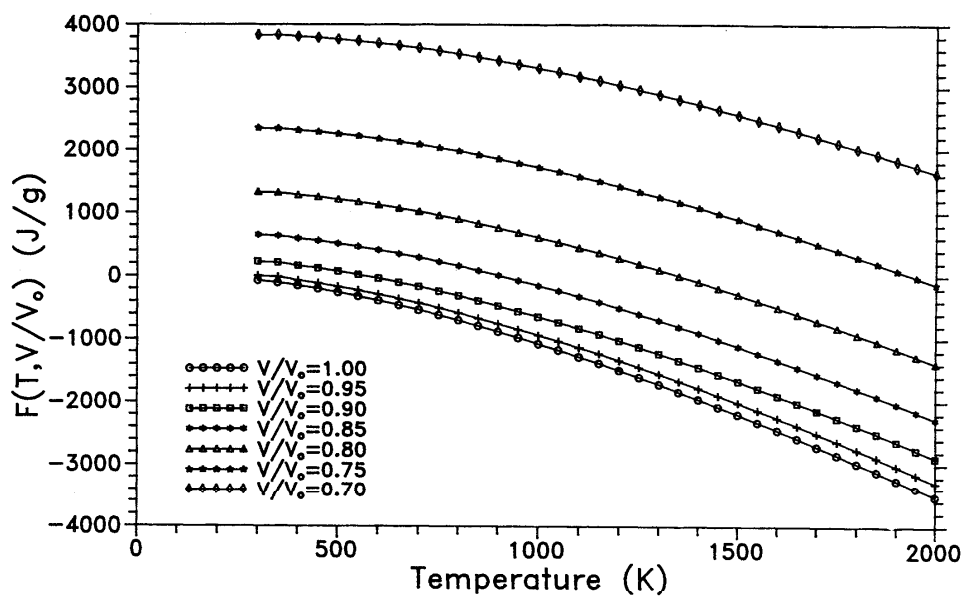
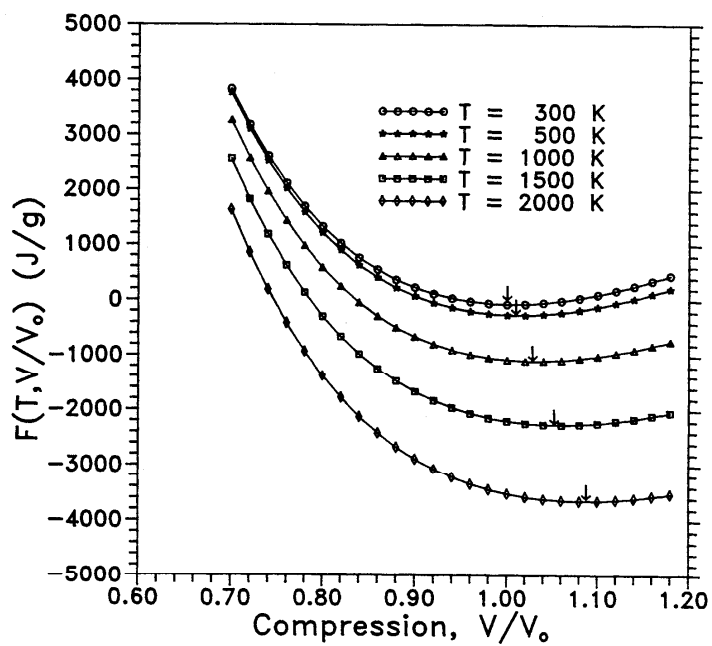FIG. 3. The isochoric plots of Helmholtz energy $F_\chi$ vs $T$.



FIG. 4. The isothermal plots of Helmholtz energy $F_T$ vs $\chi$. The arrows indicate the
position of the minimum in $F$, which establishes the equilibrium volume at
that $T$, relative to $V_0$.

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Table 7.  Helmholtz energy vs. $T$ at constant $\chi$, $F(T,V/V_o)$

| $T$ (K) | $F(T,1.0)$ | $F(T,0.95)$ | $F(T,0.90)$ | $F(T,0.85)$ (J/g) | $F(T,0.80)$ | $F(T,0.75)$ | $F(T,0.70)$ |
|---|---|---|---|---|---|---|---|
| 300 | −74 | 0 | 220 | 650 | 1330 | 2350 | 3830 |
| 350 | −111 | −19 | 210 | 630 | 1320 | 2340 | 3830 |
| 400 | −155 | −74 | 160 | 590 | 1280 | 2310 | 3810 |
| 450 | −206 | −120 | 120 | 550 | 1250 | 2290 | 3790 |
| 500 | −263 | −170 | 70 | 510 | 1210 | 2260 | 3760 |
| 550 | −325 | −230 | 20 | 460 | 1170 | 2220 | 3740 |
| 600 | −393 | −290 | −40 | 410 | 1120 | 2180 | 3700 |
| 650 | −465 | −360 | −110 | 350 | 1070 | 2140 | 3660 |
| 700 | −541 | −430 | −170 | 290 | 1010 | 2090 | 3620 |
| 750 | −622 | −510 | −240 | 220 | 950 | 2030 | 3580 |
| 800 | −706 | −590 | −320 | 160 | 890 | 1980 | 3530 |
| 850 | −794 | −670 | −400 | 82 | 820 | 1920 | 3480 |
| 900 | −886 | −760 | −480 | 6 | 750 | 1850 | 3420 |
| 950 | −980 | −850 | −560 | −74 | 680 | 1790 | 3360 |
| 1000 | −1080 | −940 | −650 | −160 | 610 | 1720 | 3300 |
| 1050 | −1180 | −1040 | −740 | −240 | 530 | 1650 | 3240 |
| 1100 | −1280 | −1140 | −840 | −330 | 440 | 1570 | 3170 |
| 1150 | −1390 | −1240 | −930 | −420 | 360 | 1490 | 3100 |
| 1200 | −1500 | −1340 | −1030 | −510 | 270 | 1420 | 3030 |
| 1250 | −1610 | −1450 | −1130 | −610 | 180 | 1330 | 2960 |
| 1300 | −1720 | −1560 | −1230 | −710 | 93 | 1250 | 2880 |
| 1350 | −1840 | −1670 | −1340 | −810 | −1 | 1160 | 2800 |
| 1400 | −1960 | −1780 | −1450 | −910 | −97 | 1070 | 2720 |
| 1450 | −2080 | −1900 | −1560 | −1010 | −190 | 980 | 2640 |
| 1500 | −2200 | −2020 | −1670 | −1120 | −290 | 890 | 2560 |
| 1550 | −2330 | −2140 | −1790 | −1230 | −400 | 800 | 2470 |
| 1600 | −2450 | −2260 | −1900 | −1340 | −500 | 700 | 2390 |
| 1650 | −2580 | −2380 | −2020 | −1450 | −610 | 600 | 2300 |
| 1700 | −2710 | −2500 | −2140 | −1560 | −710 | 500 | 2210 |
| 1750 | −2840 | −2630 | −2260 | −1680 | −820 | 400 | 2110 |
| 1800 | −2980 | −2760 | −2380 | −1800 | −930 | 300 | 2020 |
| 1850 | −3110 | −2890 | −2510 | −1910 | −1040 | 200 | 1920 |
| 1900 | −3250 | −3020 | −2630 | −2030 | −1160 | 89 | 1830 |
| 1950 | −3390 | −3160 | −2760 | −2160 | −1270 | −19 | 1730 |
| 2000 | −3530 | −3290 | −2890 | −2280 | −1390 | −130 | 1630 |

Table 8.  Entropy vs. $T$ at constant $P$, $S(T,P)$

| $T$ (K) | $S(T,0)$ | $S(T,20)$ | $S(T,50)$ | $S(T,80)$ (J g$^{-1}$ K$^{-1}$) | $S(T,100)$ | $S(T,125)$ |
|---|---|---|---|---|---|---|
| 300 | 0 6743 | 0.54 | 0.42 | 0.35 | 0.31 | 0.26 |
| 350 | 0.824 | 0 68 | 0.55 | 0.47 | 0.42 | 0.38 |
| 400 | 0.962 | 0.81 | 0.68 | 0.59 | 0.54 | 0.49 |
| 450 | 1.089 | 0.94 | 0.80 | 0.70 | 0.65 | 0.60 |
| 500 | 1.207 | 1.05 | 0.91 | 0.81 | 0.76 | 0.71 |
| 550 | 1.316 | 1.16 | 1.01 | 0.91 | 0.86 | 0.81 |
| 600 | 1.417 | 1.26 | 1.11 | 1.01 | 0.96 | 0.90 |
| 650 | 1.512 | 1.35 | 1.20 | 1.10 | 1.05 | 0.99 |
| 700 | 1.600 | 1.44 | 1.28 | 1.18 | 1.13 | 1.08 |
| 750 | 1.684 | 1.52 | 1.37 | 1.27 | 1.21 | 1.16 |
| 800 | 1.762 | 1.60 | 1.44 | 1.34 | 1.29 | 1.24 |
| 850 | 1.837 | 1.67 | 1.52 | 1.41 | 1.36 | 1.31 |
| 900 | 1.908 | 1.74 | 1.59 | 1.48 | 1.43 | 1.38 |
| 950 | 1.976 | 1.81 | 1.65 | 1.55 | 1.50 | 1.44 |
| 1000 | 2.040 | 1.87 | 1.72 | 1.61 | 1.56 | 1.51 |
| 1050 | 2.102 | 1.93 | 1.78 | 1.68 | 1.62 | 1.57 |
| 1100 | 2.161 | 1.99 | 1.84 | 1.73 | 1.68 | 1.63 |
| 1150 | 2.218 | 2.05 | 1.89 | 1.79 | 1.74 | 1.69 |
| 1200 | 2 273 | 2.10 | 1.95 | 1.85 | 1.79 | 1.74 |
| 1250 | 2 325 | 2.16 | 2.00 | 1.90 | 1.85 | 1.79 |
| 1300 | 2.376 | 2.21 | 2.05 | 1.95 | 1.90 | 1.84 |
| 1350 | 2.426 | 2.26 | 2.10 | 2.00 | 1.95 | 1.89 |
| 1400 | 2.473 | 2.31 | 2.15 | 2.05 | 2.00 | 1.94 |
| 1450 | 2.519 | 2.35 | 2.20 | 2 09 | 2.04 | 1.99 |
| 1500 | 2.564 | 2.40 | 2.24 | 2 14 | 2.09 | 2.03 |
| 1550 | 2.608 | 2.44 | 2.29 | 2.19 | 2.13 | 2.08 |
| 1600 | 2.650 | 2.48 | 2.33 | 2.23 | 2.17 | 2.12 |
| 1650 | 2.691 | 2.52 | 2.37 | 2.27 | 2.22 | 2.16 |
| 1700 | 2.731 | 2 57 | 2.41 | 2.31 | 2.26 | 2.21 |
| 1750 | 2.770 | 2.60 | 2.45 | 2.35 | 2.30 | 2.24 |
| 1800 | 2.808 | 2.64 | 2.49 | 2.39 | 2.34 | 2.28 |
| 1850 | 2.846 | 2.68 | 2.53 | 2.42 | 2.37 | 2.32 |
| 1900 | 2.882 | 2.72 | 2.56 | 2 46 | 2.41 | 2.36 |
| 1950 | 2.918 | 2 75 | 2.60 | 2.50 | 2.44 | 2.39 |
| 2000 | 2.953 | 2.79 | 2 63 | 2.53 | 2.48 | 2 43 |
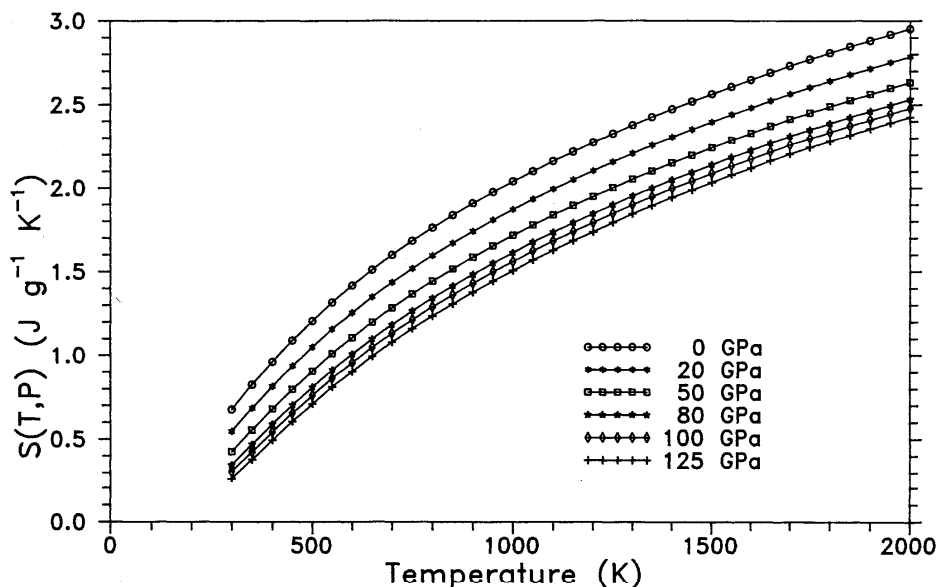
FIG. 5. The isobaric plots of entropy $S_P$ at constant $P$ vs $T$.

The value of $K_{T_0}$ used is 166.2 GPa, as discussed in the Sec. 2.6. The thermal bulk modulus correction is sufficiently small compared to $K_T$ at absolute zero to be safely ignored.

Using Eqs. (15) and (16) and values of $H$ at $P = 0$ from Garvin et al.,[7] values of $H$ vs $T$ and $P$ are found from Eq. (15) and listed in Table 9. The isotherms are listed in Table 10. The isobars of $H$ vs $T$ are shown in Fig. 6, and the isotherms of $H$ vs $P$ are shown in Fig. 7.

An alternative derivation is to use the general formula

$$H = U + PV,$$

but $U$ must be made over into a function of $P$ and $T$ (see Appendix, Sec. 6.4.).

## 2.6. The Gibbs Energy Versus Pressure and Temperature

We use

$$G(T,P) = H(T,P) - TS_P(T,P) \qquad (17)$$

to find values of the Gibbs energy. Listing of $G$ vs $T$ and $P$ is found in Table 11. The isobars of $G$ vs $T$ are found in Fig. 8.

Table 9.  Enthalpy vs. $T$ at constant $P$, $H(T,P)$

| T (K) | H(T,0) | H(T,20) | H(T,50) | H(T,80) | H(T,100) | H(T,125) |
|---|---|---|---|---|---|---|
|  |  |  | (kJ/g) |  |  |  |
| 300 | 0.1297 | 5.41 | 12.6 | 19.2 | 23.3 | 28.3 |
| 350 | 0.1782 | 5.46 | 12.6 | 19.2 | 23.4 | 28.4 |
| 400 | 0.2300 | 5.52 | 12.7 | 19.3 | 23.5 | 28.5 |
| 450 | 0.2841 | 5.58 | 12.8 | 19.4 | 23.6 | 28.6 |
| 500 | 0.3397 | 5.64 | 12.9 | 19.5 | 23.7 | 28.7 |
| 550 | 0.3970 | 5.71 | 13.0 | 19.6 | 23.8 | 28.8 |
| 600 | 0.4552 | 5.78 | 13.0 | 19.7 | 23.9 | 28.9 |
| 650 | 0.5143 | 5.85 | 13.1 | 19.8 | 24.0 | 29.0 |
| 700 | 0.5741 | 5.92 | 13.2 | 19.9 | 24.1 | 29.1 |
| 750 | 0.6346 | 5.99 | 13 3 | 20.0 | 24.2 | 29.3 |
| 800 | 0.6957 | 6.06 | 13.4 | 20.1 | 24.3 | 29.4 |
| 850 | 0.7573 | 6.13 | 13.5 | 20.2 | 24.4 | 29.5 |
| 900 | 0 8194 | 6.21 | 13 6 | 20.3 | 24.5 | 29.6 |
| 950 | 0.8819 | 6.28 | 13.6 | 20.4 | 24.6 | 29.7 |
| 1000 | 0 9448 | 6 36 | 13.7 | 20.5 | 24.8 | 29.9 |
| 1050 | 1 008 | 6.43 | 13 8 | 20.6 | 24.9 | 30.0 |
| 1100 | 1 072 | 6.51 | 13.9 | 20.7 | 25.0 | 30.1 |
| 1150 | 1 136 | 6.58 | 14 0 | 20.8 | 25.1 | 30.3 |
| 1200 | 1.200 | 6.66 | 14.1 | 20.9 | 25.2 | 30.4 |
| 1250 | 1 265 | 6 74 | 14.2 | 21.0 | 25.4 | 30.5 |
| 1300 | 1.329 | 6.82 | 14.3 | 21 2 | 25 5 | 30.7 |
| 1350 | 1 395 | 6 90 | 14.4 | 21.3 | 25.6 | 30.8 |
| 1400 | 1 460 | 6.98 | 14 5 | 21 4 | 25.7 | 31.0 |
| 1450 | 1.526 | 7 06 | 14.6 | 21.5 | 25.9 | 31.1 |
| 1500 | 1 592 | 7 14 | 14 7 | 21.6 | 26.0 | 31.2 |
| 1550 | 1 658 | 7.22 | 14.8 | 21.7 | 26.1 | 31.4 |
| 1600 | 1 725 | 7 30 | 14.9 | 21.9 | 26.3 | 31.5 |
| 1650 | 1 792 | 7.38 | 15 0 | 22.0 | 26.4 | 31.7 |
| 1700 | 1 859 | 7.46 | 15 1 | 22.1 | 26.5 | 31.8 |
| 1750 | 1.926 | 7.55 | 15.2 | 22.2 | 26.7 | 32.0 |
| 1800 | 1 994 | 7.63 | 15.3 | 22.3 | 26.8 | 32 1 |
| 1850 | 2 062 | 7.71 | 15.4 | 22.5 | 26.9 | 32 3 |
| 1900 | 2 130 | 7 80 | 15 5 | 22.6 | 27 1 | 32.4 |
| 1950 | 2 199 | 7.88 | 15 7 | 22.7 | 27.2 | 32.6 |
| 2000 | 2 268 | 7 97 | 15 8 | 22.8 | 27.3 | 32.7 |

Table 10.  Enthalpy vs. $P$ at constant $T$, $H(P,T)$

| P (GPa) | H(P,300) | H(P,500) | H(P,1000) | H(P,1500) | H(P,2000) |
|---|---|---|---|---|---|
|  |  |  | (kJ/g) |  |  |
| 0 | 0.1297 | 0.3397 | 0.9448 | 1.5918 | 2.268 |
| 5 | 1.50 | 1.72 | 2.3 | 3.0 | 3.8 |
| 10 | 2.83 | 3.05 | 3.7 | 4.4 | 5.2 |
| 15 | 4.13 | 4.36 | 5.0 | 5.8 | 6.6 |
| 20 | 5.41 | 5.64 | 6.3 | 7.1 | 8.0 |
| 25 | 6.66 | 6.90 | 7.6 | 8.5 | 9.3 |
| 30 | 7.88 | 8.13 | 8.9 | 9.7 | 10.6 |
| 35 | 9.09 | 9.35 | 10.1 | 11.0 | 11.9 |
| 40 | 10.3 | 10.5 | 11.3 | 12.2 | 13.2 |
| 45 | 11.4 | 11.7 | 12.5 | 13.5 | 14.5 |
| 50 | 12.6 | 12.9 | 13.7 | 14.7 | 15.8 |
| 55 | 13.7 | 14.0 | 14.9 | 15.9 | 16.9 |
| 60 | 14.8 | 15.1 | 16.0 | 17.1 | 18.2 |
| 65 | 16.0 | 16.3 | 17.2 | 18.2 | 19.4 |
| 70 | 17.0 | 17.3 | 18.3 | 19.4 | 20.5 |
| 75 | 18.1 | 18.4 | 19.4 | 20.5 | 21.7 |
| 80 | 19.2 | 19.5 | 20.5 | 21.6 | 22.8 |
| 85 | 20.2 | 20.6 | 21.5 | 22.7 | 24.0 |
| 90 | 21.3 | 21.6 | 22.6 | 23.8 | 25.1 |
| 95 | 22.3 | 22.6 | 23.7 | 24.9 | 26.2 |
| 100 | 23.3 | 23.7 | 24.8 | 26.0 | 27.3 |
| 105 | 24.4 | 24.7 | 25.8 | 27.1 | 28.4 |
| 110 | 25.3 | 25.7 | 26.8 | 28.1 | 29.5 |
| 115 | 26.4 | 26.7 | 27.8 | 29.2 | 30.6 |
| 120 | 27.4 | 27.7 | 28.9 | 30.2 | 31.7 |
| 125 | 28.3 | 28.7 | 29.9 | 31.2 | 32.7 |
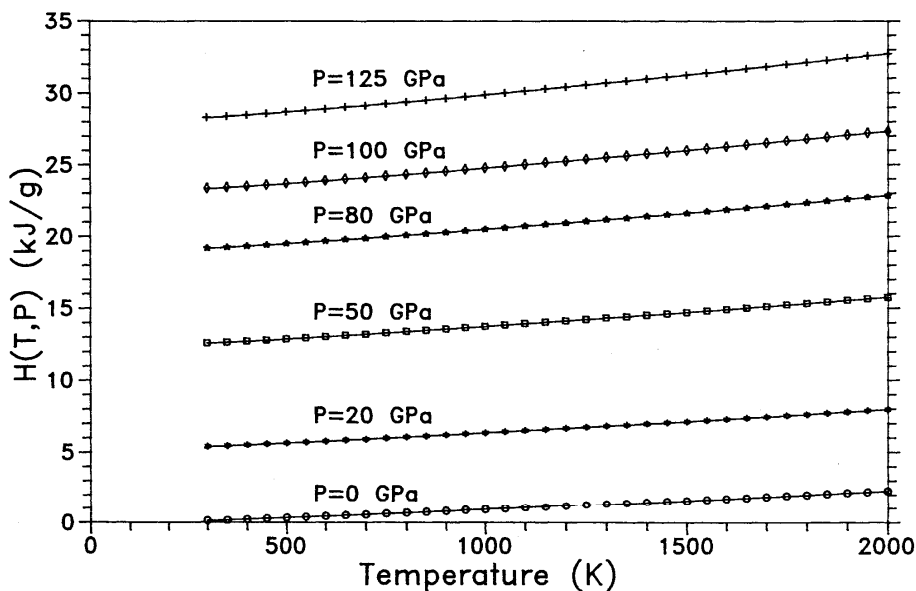
FIG. 6. The isobaric plots of enthalpy $H_P$ at constant $P$ vs $T$

## 2.7. Evidence for the Quasiharmonic Model for MgO out to 2000 K

The variation of $C_P$ with $T$ at constant pressure ($P = 1$ atmosphere) and the computed $C_V$ at constant volume ($\chi = 1$) with $T$, as well as the variation of entropy, both $S_P$ and $S_\chi$ ($P = 1$ atmosphere; $\chi = 1$), are shown in Fig. 9. We find $C_V$ to be classical with little evidence of anharmonicity in our temperature range. That is, $(\partial C_V/\partial T)_P = 0$, indicating that in the density of states the frequencies are a function of $V$ but not of $T$ at least up to about 2000 K.

## 3. The Strategy of the Calculations

### 3.1. Zero Pressure Data

In general we followed the principle of the method of computing thermodynamic functions outlined by Slater.[12] Laboratory data on $\alpha$, $C_P$, $K_S$, and $(\partial K_S/\partial T)_P$ were each represented by polynomials, and data for each of the quantities was computed at 10 degree temperature intervals from 300 to 2000 K and then stored in a database. Then, $\gamma$, $\delta_T$, $C_V$, and $\alpha K_T$ were computed at 10 degree temperature intervals and stored, and the following were computed
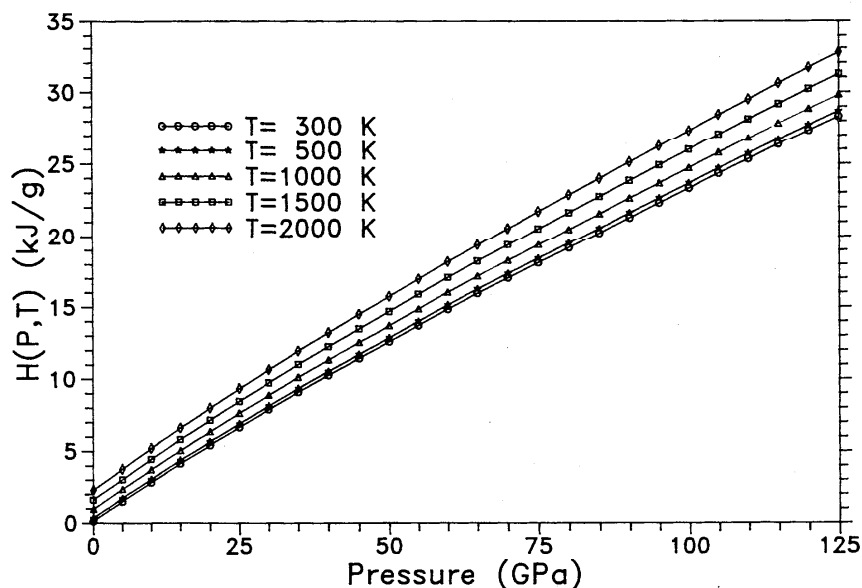


FIG. 7 The isothermal plots of enthalpy $H_P$ at constant $T$ vs $P$.

Table 11. The Gibbs energy vs. T at constant P, G(T,P)

| T (K) | G(T,0) | G(T,20) | G(T,50) | G(T,80) | G(T,100) | G(T,125) |
|---|---|---|---|---|---|---|
| | | | (kJ/g) | | | |
| 300 | -0.0726 | 5.24 | 12.5 | 19.1 | 23.2 | 28.2 |
| 350 | -0.1101 | 5.22 | 12.5 | 19.1 | 23.3 | 28.3 |
| 400 | -0.1547 | 5.19 | 12.4 | 19.1 | 23.3 | 28.3 |
| 450 | -0.2060 | 5.16 | 12.4 | 19.1 | 23.3 | 28.3 |
| 500 | -0.2635 | 5.12 | 12.4 | 19.1 | 23.3 | 28.3 |
| 550 | -0.3266 | 5.07 | 12.4 | 19.1 | 23.3 | 28.3 |
| 600 | -0.3949 | 5.02 | 12.4 | 19.1 | 23.3 | 28.4 |
| 650 | -0.4682 | 4.97 | 12.3 | 19.1 | 23.3 | 28.4 |
| 700 | -0.5459 | 4.91 | 12.3 | 19.0 | 23.3 | 28.4 |
| 750 | -0.6280 | 4.85 | 12.3 | 19.0 | 23.3 | 28.4 |
| 800 | -0.7142 | 4.78 | 12.2 | 19.0 | 23.3 | 28.4 |
| 850 | -0.8042 | 4.71 | 12.2 | 19.0 | 23.3 | 28.4 |
| 900 | -0.8978 | 4.64 | 12.1 | 18.9 | 23.2 | 28.4 |
| 950 | -0.9950 | 4.56 | 12.1 | 18.9 | 23.2 | 28.4 |
| 1000 | -1.095 | 4.48 | 12.0 | 18.9 | 23.2 | 28.4 |
| 1050 | -1.199 | 4.40 | 12.0 | 18.8 | 23.2 | 28.4 |
| 1100 | -1.306 | 4.32 | 11.9 | 18.8 | 23.2 | 28.3 |
| 1150 | -1.415 | 4.23 | 11.8 | 18.8 | 23.1 | 28.3 |
| 1200 | -1.527 | 4.14 | 11.8 | 18.7 | 23.1 | 28.3 |
| 1250 | -1.642 | 4.04 | 11.7 | 18.7 | 23.1 | 28.3 |
| 1300 | -1.760 | 3.95 | 11.6 | 18.6 | 23.0 | 28.3 |
| 1350 | -1.880 | 3.85 | 11.6 | 18.6 | 23.0 | 28.3 |
| 1400 | -2.002 | 3.75 | 11.5 | 18.5 | 22.9 | 28.2 |
| 1450 | -2.127 | 3.65 | 11.4 | 18.5 | 22.9 | 28.2 |
| 1500 | -2.254 | 3.54 | 11.4 | 18.4 | 22.9 | 28.2 |
| 1550 | -2.384 | 3.44 | 11.3 | 18.4 | 22.8 | 28.2 |
| 1600 | -2.515 | 3.33 | 11.2 | 18.3 | 22.8 | 28.1 |
| 1650 | -2.649 | 3.22 | 11.1 | 18.2 | 22.7 | 28.1 |
| 1700 | -2.784 | 3.10 | 11.0 | 18.2 | 22.7 | 28.1 |
| 1750 | -2.922 | 2.99 | 10.9 | 18.1 | 22.6 | 28.0 |
| 1800 | -3.061 | 2.87 | 10.9 | 18.0 | 22.6 | 28.0 |
| 1850 | -3.202 | 2.76 | 10.8 | 18.0 | 22.5 | 28.0 |
| 1900 | -3.346 | 2.64 | 10.7 | 17.9 | 22.5 | 27.9 |
| 1950 | -3.491 | 2.52 | 10.6 | 17.8 | 22.4 | 27.9 |
| 2000 | -3.637 | 2.39 | 10.5 | 17.8 | 22.4 | 27.9 |

as a function of $T$ and stored at 10 degree intervals: $\int_{300}^{T} (C_P/T)\, dT$; $\int_{300}^{T} C_P\, dT$; $\int_{300}^{T} C_V\, dT$; $\int_{300}^{T} (C_V/T)\, dT$; $\delta_T = -(1/\alpha K_T)(\partial K_T/\partial T)_{P=0}$; and $\delta_S = -(1/\alpha K_S) \times (\partial K_S/\partial T)_{P=0}$.

The entropy at 300 K (a constant of integration at $V/V_0 = 1$) was found by integrating $\int_0^{300}[(C_P - C_V)/T]\, dT$, and comparing this with the measured entropy at $P = 0$ and $T = 300$ K. The value of $\rho/\rho_0 = 1.0127 \int_{300}^{T} \alpha dT$ was com-

puted from 300 to $T$ and then stored. The values of entropy and internal energy at 300 K were both calculated for constant $V$. Values of constant pressure entropy and enthalpy were copied from the Garvin et al.[7] tables.

## 3.2. Compression Data at Absolute Zero

Using the values of $K_{T_0} = 166.2$ GPa, $K_{T_0}' = 4.07$, and $\rho_0 = 3.6312$ (all representing estimated values for MgO at absolute zero), the pressure was calculated for $\chi = V/V_0$ intervals of 0.001, as shown in Table 12. The inverse calculation, values of $\chi$ for integral change in $P$, is shown in Table 13.

The values of $\int_0^P P_0\, d\chi$ were calculated for insertion into the internal energy [see Eq. (12)], and listed in Table 13. The function $\int_{V_0}^{V} K_T\, d\chi$ was evaluated for each isotherm $T^*$, using Eq. (21) for $K_T(V)$ where the lower limit $V_0$ is the volume where $P = 0$ at temperature $T^*$ for values of $P$ at intervals of 5 GPa, as listed in Table 13. The values of $\int_{V_0}^{V} K_T\, dV$, and of $\int_{V_0}^{V} P_0\, dV$, for the limits $V_0 = V(T^*,P = 0)$ and $V = V(T^*,P)$ were computed and stored for use in the calculations of $U$ and $H$.

## 3.3. The Original Experimental Data and Probable Errors

Recent measurements[9] of $K_S$ up to 1800 K confirmed the high temperature extrapolations up to 1800 K made by Sumino et al.[5] on measurements taken to 1300 K. Isaak et al.'s data[9] on $K_T$ were used over the whole temperature range.

The values of $C_P$, $S$, and $H$ used in these computations were taken from the thermodynamic tables of Garvin et al.[7] Their data give $C_P$, $S$, and $H$ up to 2000 K. The values of $C_P - C_V$ for MgO were tabled by Barron et al.,[10] from which the value of $U(300,V/V_0 = 1)$ was computed using the tabled $U(300,P = 0)$ value.
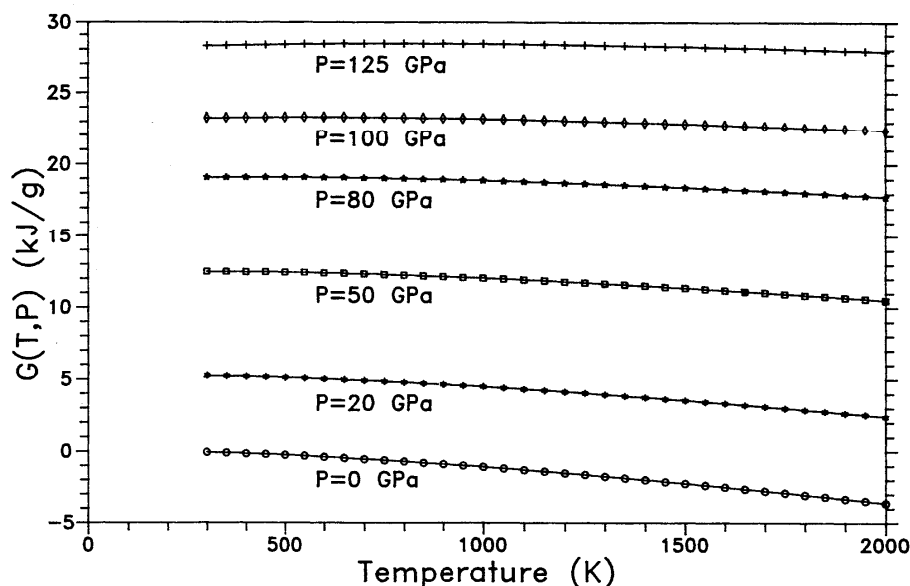


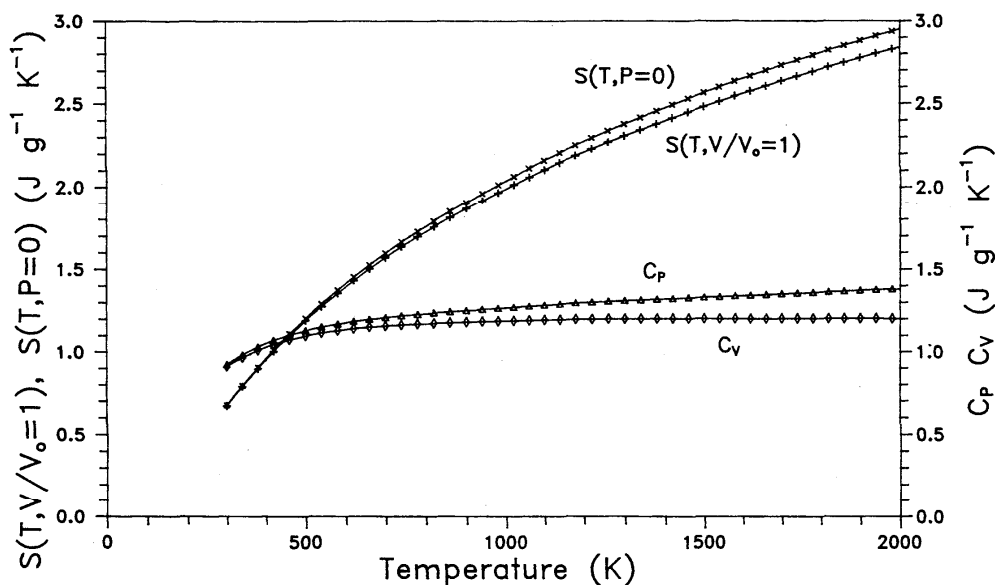FIG 8. The isobaric plots of Gibbs energy $G$ at constant $P$ vs $T$.

FIG 9. Comparison of entropy at constant $P$ and constant $\chi$, versus $T$, and the comparison of $C_P$ and $C_V$ vs $T$

Values of $K_T(0)$ and $K'_T$ appropriate to absolute zero were needed, and computed as follows:

$$\frac{K_S(300)}{K_S(0)} = \left(\frac{\rho(0)}{\rho(300)}\right)^{K'_S},$$

where $\rho(0) = 1.0127\rho(300)$. The experiments of Jackson and Niesler[13] show that for MgO, $K_S(300) = 162.5$ GPa, and $K'_S = 4.13$. These lead to the following values:

$$K_T(0) = 166.2 \text{ GPa}, \quad K_T(300) = 160.5 \text{ GPa},$$

$$K'_T = 4.17.$$

Transformations above from the adiabatic to isothermal bulk modulus pressure derivative use the following (see Spetzler et al.[14]):

$$K'_T = K'_S(1 + \alpha\gamma T)^{-1}$$

$$- \frac{K_S T}{(1 + \alpha\gamma T^2)}\left(\gamma\frac{\partial\alpha}{\partial P}\bigg|_T + \alpha\frac{\partial\gamma}{\partial P}\bigg|_T\right).$$

Table 12  The pressure and the function $\int Pd(V/V_o)$ vs $\chi$

| $\chi = V/V_o$ | $P(V/V_o)$ (GPa) | $\int_1^{(V/V_o)} Pd(V/V_o)$ (GPa) | $\chi = V/V_o$ | $P(V/V_o)$ (GPa) | $\int_1^{(V/V_o)} Pd(V/V_o)$ (GPa) |
|---|---|---|---|---|---|
| 1 105 | -13.4800 | 0 7709 | 0 890 | 24.7070 | 1 2293 |
| 1.100 | -12.9894 | 0.7047 | 0.885 | 26.2091 | 1.3566 |
| 1 095 | -12.4861 | 0.6410 | 0.880 | 27.7522 | 1 4914 |
| 1.090 | -11 9697 | 0.5799 | 0.875 | 29.3372 | 1.6341 |
| 1 085 | -11.4398 | 0.5214 | 0.870 | 30.9665 | 1.7848 |
| 1 080 | -10 8962 | 0.4655 | 0.865 | 32 6402 | 1.9437 |
| 1.075 | -10.3384 | 0.4124 | 0.860 | 34.3603 | 2.1111 |
| 1.070 | -9.7663 | 0.3622 | 0 855 | 36.1283 | 2.2872 |
| 1 065 | -9 1791 | 0.3148 | 0.850 | 37.9453 | 2 4723 |
| 1 060 | -8 5767 | 0 2704 | 0 845 | 39 8126 | 2.6666 |
| 1 055 | -7.9586 | 0.2291 | 0 840 | 41 7326 | 2 8704 |
| 1.050 | -7 3245 | 0 1909 | 0.835 | 43 7065 | 3 0839 |
| 1.045 | -6.6739 | 0.1559 | 0.830 | 45 7357 | 3 3074 |
| 1 040 | -6 0063 | 0.1242 | 0.825 | 47 8222 | 3 5412 |
| 1 035 | -5 3214 | 0 0959 | 0.820 | 49.9680 | 3 7856 |
| 1.030 | -4 6186 | 0 0710 | 0 815 | 52 1746 | 4.0409 |
| 1 025 | -3.8976 | 0.0497 | 0.810 | 54 4444 | 4 3074 |
| 1 020 | -3 1577 | 0 0321 | 0 805 | 56 7793 | 4 5855 |
| 1 015 | -2.3985 | 0.0182 | 0 800 | 59 1812 | 4.8754 |
| 1.010 | -1.6195 | 0 0081 | 0 795 | 61.6522 | 5 1775 |
| 1.005 | -0 8201 | 0.0021 | 0 790 | 64.1949 | 5.4921 |
| 1 000 | 0 0000 | 0 0000 | 0 785 | 66 8121 | 5 8197 |
| 0.995 | 0 8418 | 0.0021 | 0 780 | 69.5049 | 6.1605 |
| 0 990 | 1.7054 | 0 0084 | 0.775 | 72 2769 | 6 5150 |
| 0.985 | 2.5922 | 0.0191 | 0.770 | 75.1304 | 6 8836 |
| 0.980 | 3.5019 | 0 0343 | 0 765 | 78 0684 | 7 2666 |
| 0.975 | 4.4356 | 0 0542 | 0 760 | 81.0934 | 7.6646 |
| 0.970 | 5.3939 | 0.0788 | 0 755 | 84.2082 | 8.0779 |
| 0 965 | 6.3774 | 0 1082 | 0 750 | 87.4168 | 8 5070 |
| 0.960 | 7.3871 | 0.1427 | 0.745 | 90 7217 | 8 9523 |
| 0.955 | 8.4236 | 0.1823 | 0.740 | 94.1260 | 9 4144 |
| 0.950 | 9 4873 | 0.2271 | 0.735 | 97 6336 | 9.8938 |
| 0 945 | 10.5792 | 0 2774 | 0.730 | 101 2482 | 10.3909 |
| 0.940 | 11.7004 | 0.3331 | 0.725 | 104 9734 | 10.9064 |
| 0 935 | 12 8516 | 0.3946 | 0 720 | 108.8132 | 11 4407 |
| 0 930 | 14.0334 | 0 4619 | 0 715 | 112 7713 | 11.9946 |
| 0 925 | 15.2468 | 0.5351 | 0 710 | 116.8524 | 12 5685 |
| 0 920 | 16 4925 | 0.6145 | 0 705 | 121 0608 | 13 1631 |
| 0 915 | 17 7723 | 0 7002 | 0 700 | 125 4013 | 13 7791 |
| 0.910 | 19.0861 | 0.7924 | 0 695 | 129 8786 | 14 4171 |
| 0 905 | 20 4353 | 0.8912 | 0.690 | 134 4976 | 15 0780 |
| 0.900 | 21 8212 | 0 9968 | 0 685 | 139.2634 | 15.7623 |
| 0 895 | 23 2446 | 1 1095 | 0 680 | 144 1823 | 16 4710 |

Table 13  The compression, $\chi = V/V_o$, and the functions $\int \chi dP$ and $\int Pd\chi$ vs $P$

| $P$ (GPa) | $\chi = V/V_o$ | $\int_0^P \chi dP$ (GPa) | $\int_1^\chi Pd\chi$ (GPa) |
|---|---|---|---|
| 0 | 1.000 | 0 0000 | 0 0000 |
| 5 | 0 972 | 4 9284 | 0.0684 |
| 10 | 0 948 | 9 7261 | 0 2466 |
| 15 | 0 926 | 14 4090 | 0.5200 |
| 20 | 0 907 | 18.9896 | 0.8509 |
| 25 | 0 889 | 23 4779 | 1.2542 |
| 30 | 0 873 | 27 8822 | 1 6934 |
| 35 | 0 858 | 32 2095 | 2 1805 |
| 40 | 0 845 | 36 4658 | 2 6666 |
| 45 | 0 832 | 40 6561 | 3.2168 |
| 50 | 0 820 | 44 7850 | 3 7856 |
| 55 | 0 809 | 48 8565 | 4 3621 |
| 60 | 0 798 | 52 8739 | 4 9948 |
| 65 | 0 788 | 56 8405 | 5 6216 |
| 70 | 0 779 | 60 7591 | 6 2303 |
| 75 | 0.770 | 64 6321 | 6 8836 |
| 80 | 0 762 | 68 4619 | 7 5036 |
| 85 | 0 754 | 72 2505 | 8.1624 |
| 90 | 0 746 | 75 9999 | 8 8619 |
| 95 | 0 739 | 79 7118 | 9.5089 |
| 100 | 0 732 | 83 3877 | 10 1899 |
| 105 | 0 725 | 87.0292 | 10.9064 |
| 110 | 0 719 | 90.6377 | 11 5500 |
| 115 | 0 712 | 94 2145 | 12 3365 |
| 120 | 0 706 | 97 7606 | 13.0425 |
| 125 | 0 701 | 101 2773 | 13 6542 |
| 130 | 0 695 | 104 7655 | 14 4172 |

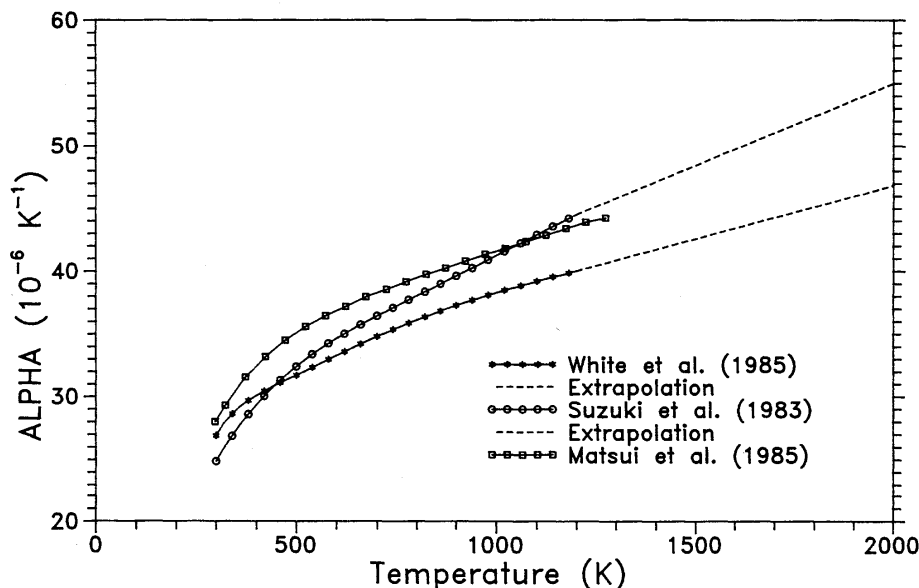FIG 10  The volume thermal expansivity $\alpha$ of $Mg_2SiO_4$, according to three experimentalists: Suzuki et al.,[15] White et al.,[16] and Matsui and Manghnani[17]; data taken to 1200–1300 K, extrapolations of the upper and lower cases taken to 2000 K.

From this equation we get

$$K'_T = (1 + \alpha\gamma T)^{-1}[K'_S + \alpha\gamma T(\delta_T + q)], \qquad (18)$$

where

$$\delta_r = -K_T \frac{\partial \ln \alpha}{\partial P}\bigg|_T, \quad q = \frac{\partial \ln \gamma}{\partial \ln V}\bigg|_T = -\left(\frac{\rho}{\gamma}\right)\frac{\partial \gamma}{\partial P}\bigg|_T,$$

$$K_T = K_S(1 + \alpha\gamma T)^{-1}.$$

Analysis[9] of the measurements shows that $\delta_T = 5.48$ for MgO, and $q = d \ln \gamma/d \ln V = 1.5$. Thus we find from Eq. (23) that $K'_T$ changes from 4.13 at 300 K to 4.17 at 0 K, which is used in Eqs. (7) and (16).

Of importance to the calculation of the thermodynamic functions is the parameter $w$ given by Eq. (2); $w = (\partial K_T/\partial T)_V$. In general this is a small number compared to $(\partial K_T/\partial T)_P$ (see Table 2), but for some solids it may be temperature dependent. Its $P = 0$ value is computed from the measurements given by the balance between $(\partial K_T/\partial T)_P$ and $\alpha K_T(\partial K_T/\partial P)_T$, the first term being negative and the second positive. If $(\partial K_T/\partial T)_V$ is zero, making Eq. (2) zero, than we know from a thermodynamic identity that $(\partial \alpha K_T/\partial V)_T$ is zero. But in general Eq. (2) is not zero, although it is often a small quantity. Also of importance is the value of the temperature dependence of $(\partial K_T/\partial P)_T$, or $(d^2K_T/dPdT)$. For MgO, Spetzler[14] found $d^2K_T/dTdP = 0$ up to 800 K. We assumed this continued up to 2000 K.

For MgO we find that $w$ is in the range 2–10 MPa/K, or less than 1% of the value of $(\partial K_T/\partial T)_P$, and it is negative. This means that the error arising from $w$ is negligible, even if $(\partial K_T/\partial P)_T$ turns out to be a function of $T$ at high pressure.

The most serious uncertainty in the application of the equations presented in this paper to other solids arises from the uncertainty in the thermal expansivity at high $T$. The situation on the agreement on $\alpha$ is not bad for MgO, and so uncertainty in $\alpha$ does not affect these results. But the thermal expansivity reports on $Mg_2SiO_4$, for example, illustrate that in general there is a problem in applying these equations to other solids at high temperature.

The data for high-temperature thermal expansivity of $Mg_2SiO_4$ are shown in Fig. 10 for these experimentalists: Suzuki et al.[15]; White et al.[16]; and Matsui and Manghnani.[17] As can be seen the extrapolations of these three thermal expansivities lead to quite differing values of $\alpha$ at 2000 K. This would lead to uncertainty in $\gamma$, $\alpha K_T$, and entropy. The most serious problem in evaluating the thermodynamic functions in the high-temperature regime (near 2000 K) is the dearth of information on $\alpha$ in this region. In general, an error of 20% in $\alpha$ at 2000 K, as shown in Fig.10, would lead to a 7% error in entropy at $\chi = 0.7$ and $T = 2000$ K, but to virtually no error at $\chi = 1$. An error of 20% in $\alpha$ at 2000 K would lead to about 1% error in $U$ and $H$, since these functions are dominated by the integrals of the equation of state, and $\alpha$ affects only the density.

## 4. Acknowledgments

## 5. References

[1]O. L. Anderson, J Geodyn 1, 185 (1984).
[2]T Goto and O. L Anderson, Rev. Sci. Instrum 59, 1405 (1988)