Equation of State of Minerals for Thermodynamic Databases Used in Petrology


* Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia; e-mail: taras@iem.ac.ru

** Institute of Earth Sciences, Uppsala University, S-75236, Uppsala, Sweden
Received May 14, 1998

Abstract—On the basis of the $P$–$T$ partition function, Landau theory of phase transitions, and thermodynamics of solid solutions, an equation of state for minerals was derived. It is based on the standard principle of the minimization of the Gibbs thermodynamic potential ($G$) of a mineral in an equilibrium state. For a substance with a $\lambda$-transition, the Gibbs free energy is defined as a function of temperature ($T$), pressure ($P$), and ordering parameter ($X_o$). The equilibrium mole fraction of ordered particles ($X_o$) is determined from the condition $G = f(P, T, X_o) = \min$. Application to the system coesite–stishovite–$\alpha$-quartz–$\beta$-quartz demonstrated that the equation allows the representation of experimental data within errors and shows good extrapolation characteristics. The equation is efficient for designing internally consistent thermodynamic databases.

INTRODUCTION

The equations of state provide a basis for the description of substance behavior at high temperature and pressure. Hence, they are equally important for petrologists and Earth physics specialists (e.g., Zharkov and Kalinin, 1968; Polyakov and Kusov, 1994). In a recent exhaustive review, Saxena (1992) discussed the physical principles of equations of state and modern approaches to their derivation and application (see also Polyakov and Kusov, 1994).

A number of publications are dedicated to the derivation of an equation of state for various crystalline phases from their vibration spectra (Saxena, 1992; Polyakov and Kusov, 1994). Unfortunately, the vibration spectra of the majority of minerals are extremely complex and poorly understood. Because of this, for the construction of internally consistent thermodynamic databases, petrologists (Karpov et al., 1976; Helgeson et al., 1978; Berman, 1988; Holland and Powell, 1990) and internally consistent systems of mineralogical thermometers and barometers (Perchuk, 1969, 1989a, 1989b, 1990; Gerya and Perchuk, 1990, 1992, 1994; INFOREX-4.0: Perchuk and Gerya, 1992) resulted in a considerable advance in the understanding of the physicochemical conditions of formation of igneous (e.g., Frolova et al., 1992) and metamorphic (e.g., Perchuk et al., 1989, 1994, 1995, 1996, 1998) rocks.

One drawback of such a petrologic approach is the poor extrapolation characteristics of the power expansion series (Berman, 1988; Richet et al., 1992) for the description of the thermodynamic properties of minerals and fluids. Perchuk and Gerya (1997) used the Landau theory of phase transitions together with the Margules thermodynamic formalism to derive a relatively simple and efficient equation of state for fluids in a very wide range of $P$–$T$ parameters. This equation adequately reproduces the $P$–$V$–$T$ properties of gases in the experimentally studied region and shows good extrapolation characteristics. A similar approach can be used for crystalline phases, which is demonstrated below by the example of SiO$_2$.
DERIVATION OF THE GIBBS FREE ENERGY EQUATION FOR MINERALS

In general, the Gibbs potential, $G$ of any substance is a function of temperature, $T$, pressure, $P$, and an ordering parameter, $\eta$. The equilibrium value of $\eta$ at $P$ and $T$ corresponds to the minimum of the Gibbs free energy:

$$ G = f(P, T, \eta) = \min, $$

where $\eta$ is the dimensionless parameter quantitatively (e.g., from 0 to 1) characterizing a change in the structure of the substance due to a phase transition (Landau and Lifshitz, 1995, pp. 502–572). The choice of the ordering parameter depends on the nature of the substance. For example, for minerals of a variable composition, it is a function of component concentrations on certain structural positions.

In a crystalline substance, the atoms are closely packed and oscillate near definite equilibrium positions. Such a system possesses $3N$ vibrational degrees of freedom, where $N$ is the number of atoms. Mechanically, it may be regarded as a combination of $3N$ independent quantum oscillators, each corresponding to a separate independent oscillation (Landau and Lifshitz, 1995). The equilibrium value of the Gibbs free energy of the system of quantum oscillators under constant $T$ and $P$ can be calculated on the basis of the $T$–$P$ partition function (Boguslavskii, 1961; Kubo, 1965):

$$ G = -kT \ln(Y), \quad \text{(2)} $$

where

$$ Y = \sum_{i=0}^{\infty} \exp\left\{-\frac{[E_i(V) + PV]}{kT}\right\} dV, \quad \text{(3)} $$

$Y$ is the statistical sum, $k$ is Boltzmann’s constant, $V$ is the volume of the system, and $E_i(V)$ is the energy of the system in the $i$th quantum state as a function of volume. The exact form of the function $E_i(V)$ is not known and empirical approximations are used for its representation. If in any $i$th quantum state at a given $P$, there is a unique value of the system volume $V_i(P)$ with the non-zero probability, then

$$ \exp\left\{-\frac{[E_i(V) + PV]}{kT}\right\} dV = \exp\left\{-\frac{H_i(P)}{kT}\right\}, \quad \text{(4)} $$

where

$$ H_i(P) = E_i(P) + PV_i(P), $$

$$ E_i(P) = E_i[V_i(P)], $$

$H_i(P)$, $E_i(P)$, and $V_i(P)$ are the enthalpy (more precisely, its microscopic analog), energy, and volume of the system, respectively, in the $i$th quantum state as a function of $P$. Let us introduce then the effective volume $V_i(P)$ and corresponding $H_i(P)$ and $E_i(P)$, such that equation (4) will hold if in the $i$th quantum state at a given $P$ the fluctuations of the system volume $V$ are allowed relative to $V_i(P)$. Substituting equation (4) simplifies statistical sum (3) to

$$ Y = \sum_{i} \exp[-H_i(P)/kT]. \quad \text{(5)} $$

Normalizing partition function (2) relative to the state of zero-point vibrations, we get

$$ G = G_0(P) - kT \ln(Y_0), \quad \text{(6)} $$

where

$$ Y_0 = \sum_{i} \exp[-\Delta H_i(P)/kT], $$

$$ \Delta H_i(P) = H_i(P) - H_0(P) = \Delta E_i(P) + P \Delta V_i(P), $$

$$ H_0(P) = E_0(P) + PV_0(P), $$

$$ \Delta E_i(P) = E_i(P) - E_0(P), $$

$$ \Delta V_i(P) = V_i(P) - V_0(P), $$

$$ G_0 = H_0(P) - TS_0 $$

$Y_0$ is the statistical sum normalized with respect to the state of zero-point vibrations; $G_0(P), H_0(P), E_0(P)$, and $V_0(P)$ are the Gibbs free energy, enthalpy, energy, and volume of the system, respectively, in the state of zero-point vibrations expressed as functions of pressure; $S_0$ is the entropy of the system in the state of zero-point vibrations (according to the Nernst law, $S_0 = 0$ for ordered crystals); $\Delta H_i(P), \Delta E_i(P)$, and $\Delta V_i(P)$ are the enthalpy, energy, and volume effects, respectively, of the transition of the system from the state of zero-point vibrations to the $i$th quantum state. Taking into account the independence of oscillators, $\Delta H_i(P), \Delta E_i(P)$, and $\Delta V_i(P)$ in (6) may be expanded with respect to the number of oscillators and the statistical sum $Y_0$ becomes:

$$ Y_0 = \prod_{i=0}^{3N} Y_{0i}, \quad \text{(7)} $$

where

$$ Y_{0i} = \sum_{j} \exp[-\Delta H_{ij}(P)/kT], $$

$$ \Delta H_{ij}(P) = \Delta E_{ij}(P) + P \Delta V_{ij}(P), $$

$Y_{0i}$ is the statistical sum for the $i$th oscillator normalized with respect to the state of zero-point vibrations; $M$ is the number of energy levels for the $i$th oscillator; $\Delta H_{ij}(P), \Delta E_{ij}(P)$, and $\Delta V_{ij}(P)$ are the enthalpy, energy, and volume effects, respectively, of the transition of the $i$th oscillator from the state of zero-point vibrations into the $j$th energy level as functions of pressure. To calculate $Y_{0i}$, assume that each of the oscillators is characterized by the infinite number of energy levels and the val-
EQUATION OF STATE OF MINERALS

\[ \Delta H_{ij}(P) = \Delta E_{ij}(P), \quad \text{and} \quad \Delta V_{ij}(P) \] are proportional to the level index \((i) \). In this case,

\[ \Delta H_{ij}(P) = j \Delta H_{i0}(P), \quad (8) \]

\[ Y_{oi} = 1 / \{1 - \exp[\Delta H_{i0}(P)/kT]\}, \quad (9) \]

where

\[ \Delta H_{i0}(P) = \Delta E_{i0}(P) + \Delta V_{i0}(P), \]

\[ \Delta H_{ij}(P), \Delta E_{ij}(P), \text{and} \Delta V_{ij}(P) \] are enthalpy, energy, and volume effects due to transition of the \(i\)th oscillator between neighboring energy levels. According to (8) and (9), an increase in the system volume at increasing temperature at constant pressure is proportional to an increase in the number of phonons. This volume increment compensates the increase of thermal pressure, which is also proportional to the number of phonons. Thus, equations (8) and (9) are physically justified. Taking into account (9), equation (6) is recast as

\[ G = H_0(P) - TS_0 + kT \sum_i^{3N} \ln \{1 - \exp[\Delta H_{i0}(P)/kT]\}. \quad (10) \]

If \(N = vN_A\), where \(N_A\) is the Avogadro number and \(v\) is the number of atoms in the mineral unit cell, and the values of \(\Delta H_{i0}\) are identical for large groups of oscillators within the whole pressure range, equation (10) can be rearranged as

\[ \tilde{G}_S = H_S - TS_S^0 + RT \sum_i^n c_i \ln \{1 - \exp[-\Delta H_{si}/RT]\}, \quad (11) \]

where

\[ R = kN_A, \]

\[ c_i = N_i/N_A, \quad \sum_i^n c_i = 3v, \]

\[ \Delta H_{si} = N_A \Delta H_{i0}, \]

\[ R = 1.987 \text{ cal/mol/K}; H_S \text{ and } S_S^0 \] are the molar enthalpy and entropy of the mineral in the state of zero-point vibrations (assuming that \(S_S^0\) is independent of \(P\)); \(n\) is the number of oscillator groups with different vibration parameters \(\Delta H_{si}; H_i \) is the number of oscillators in the \(i\)th group; \(c_i \) is the statistical weight of the \(i\)th oscillator; \(\Delta H_{si} \) is the enthalpy effect of the transition between neighboring energy levels for the \(i\)th group (calculated for \(N_A\) oscillators).

The application of equation (11) requires incorporation of pressure dependencies of \(H_S \) and \(\Delta H_{si}. \) This can be made using the expressions

\[ H_s = H_s^0 + \int V_s dP, \quad (12) \]

\[ \Delta H_{si} = \Delta H_{si}^0 + \int \Delta V_{si} dP, \quad (13) \]

where \(P_0\) is the reference pressure; \(H_s^0\) is the molar enthalpy of the solid at 0 K and \(P_0; \Delta H_{si}^0 \) is the value of \(\Delta H_{si} \) at \(P_0; \) \(V_s \) is the molar volume of the solid at 0 K as a function of pressure; and \(\Delta V_{si} \) is the volume effect of the transition between neighboring energy levels for the \(i\)th group of oscillators as a function of pressure (calculated for \(N_A\) oscillators). Assuming that in the state of zero-point vibrations the pressure dependency of the system volume \(V_s \) is given by the Murnaghan equation, which is often used to describe the isothermic \(P-V\) properties of crystalline phase in a wide pressure range. Then,

\[ V_S = V_S^0(P_0 + \phi)^{1/5}/(P + \phi)^{1/5}, \quad (14) \]

where \(V_S^0\) is the molar volume at 0 K and \(P_0; \phi\) is the parameter characterizing the average effect of attractive interactions between atoms within the whole pressure interval; and the exponent 1/5 stems from the assumption that the potential energy of repulsive interactions between atoms is proportional to the fourth degree of the apparent volume occupied by them. The parameter \(\Delta V_{si} \) characterizes a small (\(\Delta V_{si} \ll V_s\)) change in the system volume \(V_s \) related to the energetic transitions of oscillators of the \(i\)th group. Expressing this change as an apparent small increment to \(V_s \) similar to (14) gives

\[ \Delta V_{si} = \Delta V_{si}^0(P_0 + \phi)^{1/5}/(P + \phi)^{1/5}, \quad (15) \]

where \(\Delta V_{si}^0\) is the value of the parameter at \(P_0. \) The pressure dependencies of \(H_s\) and \(\Delta H_{si} \) may be found from equations (14) and (15) taking into account (12) and (13):

\[ H_s = H_s^0 + \phi V_s^{1/5}, \quad (16) \]

\[ \Delta H_{si} = \Delta H_{si}^0 + \phi \Delta V_{si}^{1/5}, \quad (17) \]

where

\[ \Psi = 5/4(P_0 + \phi)^{1/5}[(P + \phi)^{4/5} - (P_0 + \phi)^{4/5}]. \]
Standardizing equation (11) relative to $T_0$ and $P_0$ and substituting (16) and (17) give

$$G_s = H_{T_0P_0} - TS_{T_0P_0}$$
$$+ \sum_{i=1}^{n} c_i [RT \ln (1 - \exp (-\Delta H_{si}/RT))]$$
$$- \Delta H_{si}^0 (1 - T/T_0) \exp (-\Delta H_{si}^0/RT_0)/[1$$
$$- \exp (-\Delta H_{si}^0/RT_0)] - RT \ln [1$$
$$- \exp (-\Delta H_{si}^0/RT_0)] + V_s^0 \Psi,$$

where

$$S_{T_0P_0} = -(\partial G_s/\partial T)_{T_0P_0} = S_s^0 + \sum_{i}^{n} c_i$$
$$\times \{ \Delta H_{si}^0/T_0 \exp (-\Delta H_{si}^0/RT_0)/[1$$
$$- \exp (-\Delta H_{si}^0/RT_0)] \}$$
$$+ \sum_{i}^{n} c_i \Delta H_{si}^0$$
$$\times \exp (-\Delta H_{si}^0/RT_0/[1 - \exp (-\Delta H_{si}^0/RT_0)]},$$

$$H_{T_0P_0} = G_{T_0P_0} + T_0 S_{T_0P_0} = H_s^0 + \sum_{i}^{n} c_i \Delta H_{si}^0$$
$$\times \exp (-\Delta H_{si}^0/RT_0/[1 - \exp (-\Delta H_{si}^0/RT_0)]},$$

$$G_{T_0P_0} = H_s^0 - T_0 S_{T_0P_0} + RT_0 \sum_{i}^{n} c_i$$
$$\times \ln [1 - \exp (-\Delta H_{si}^0/RT_0)] = H_{T_0P_0} - T_0 S_{T_0P_0},$$

and $G_{T_0P_0}, H_{T_0P_0},$ and $S_{T_0P_0}$ are the Gibbs free energy, enthalpy, and entropy, respectively, of one mole of the substance at the reference parameters, $T_0$ and $P_0$. As the vibration spectra of real materials are complex, the total number of parameters $c_i, \Delta H_{si}^0,$ and $\Delta V_{si}^0$ in equation (18) may be very large. For a simplified description of the thermodynamic properties of substances, equation (18) may be used with the lowest $n$ and empiric coefficients $c_i, \Delta H_{si}^0,$ and $\Delta V_{si}^0$. These coefficients may be regarded as generalized characteristics of $n$ groups of oscillators differing significantly in transition energies.

If the disordering of a mineral at increasing temperature results in a $\lambda$-transition, the dependency on the ordering parameter $\eta$ must be incorporated into equation (18). This will be made by the thermodynamic analysis of the ordering process in the most general form

$$aA + bB + \ldots + dD = \alpha,$$

where $A, B, \ldots, D$ are disordered particles; $\alpha = A_b B_d \ldots D_d$ is the ordered particle, and $a, b, \ldots, d$ are the stoichiometric coefficients. The condition of intracrystalline equilibrium for reaction (19) is given by

$$\Delta G_{ord} = RT \ln (K_{ord}) + \Delta G_{ord}^0 + \Delta G_{ord}^\alpha = 0,$$

where

$$K_{ord} = X_\alpha/(X_A^a X_B^b \ldots X_D^d),$$

$$X_A + X_B + \ldots + X_D + X_\alpha = 1,$$

$X_A, X_B, \ldots, X_D$ are the mole fractions of the disordered particles $A, B, \ldots, D$, respectively; $X_\alpha$ is the mole fraction of the ordered particle $\alpha$; $K_{ord}$ is in principle similar to the equilibrium constant of a chemical reaction similar to (19); $\Delta G_{ord}^0$ and $\Delta G_{ord}^\alpha$ are the changes of partial standard and excess energies due to reaction (19), respectively. The Gibbs free energy increment relative to the ordered state ($X_\alpha = 1$) is then

$$G_\alpha = \{ RT [X_A \ln X_A + X_B \ln (X_B) + \ldots + X_D \ln (X_D)$$
$$+ X_\alpha \ln (X_\alpha)] - \Delta G_{ord}^0 (1 - X_\alpha)/Z$$

$$+ G_{ord}^\alpha \} / [1 + X_\alpha (Z - 1)],$$

where $Z = a + b + \ldots + d$ is the normalizing factor; $G_{ord}^\alpha$ is the excess integral molar energy of mixing of ordered and disordered particles.

For the equilibrium state of the system, taking into account (18) and (21), we obtain

$$G_{s + \alpha} = G_s + c_\alpha G_\alpha = \min,$$

where $G_{s + \alpha}$ is the molar Gibbs free energy of a mineral with a $\lambda$-transition; $c_\alpha$ is the number of degrees of freedom of the mineral unit cell in ordering reaction (19), and the degree of ordering of the substance is uniquely defined by the ordering parameter $\eta = X_\alpha$.

Substituting (16) and the Margules equation, the sum of the two latter terms in equation (21) may be rewritten as

$$-\Delta G_{ord}^0 (1 - X_\alpha)/Z + G_{ord}^\alpha = -\Delta G_{ord}^0 (1 - X_\alpha)/Z$$

$$+ \sum_{j=1}^{m} W_j^G (1 - X_\alpha) (X_\alpha)^j,$$

where

$$W_j^G = W_j^H + W_j^V \Psi,$$

$$\Delta G_{ord}^\alpha = \Delta H_{ord}^\alpha + \Delta V_{ord}^\alpha \Psi,$$

$\Delta H_{ord}$ and $\Delta V_{ord}$ are the enthalpy and volume effects, respectively, of the ordering reaction at $P_0$ and $T = 0$ K; $W$ are the Margules parameters. Assume that at a certain level of oscillator energy, $m$ depending upon $X_\alpha$, there is a change in the volume and enthalpy effects of
transitions between neighboring energy levels. The statistical sums \( Y_{\alpha i} \) in (7) become

\[
Y_{\alpha i} = 1/[ \{1 - \exp(-\Delta H_{\alpha i}/kT)\}
\times [1 - \exp(-\Delta H_{\alpha i}/kT)]/[ \{1 - \exp(-\Delta H_{\alpha i}/kT)\}
+ \exp(-\Delta H_{\alpha i}/kT)] \exp(-\Delta H_{\alpha i}/kT) - \exp(-\Delta H_{\alpha i}/kT) \} ] \}
\]

(24)

where \( \Delta H_{\alpha i} \) is the enthalpy effect of energy transitions \( \Delta H_{\alpha i} \) from the zero level to level \( (m - 1) \) typical of the ordered phase; \( \Delta H_{\alpha i} \) is the enthalpy effect of energy transitions \( \Delta H_{\alpha i} \) from level \( m \) typical of the disordered phase; \( \Delta H_{\alpha i} \) is the enthalpy effect of transition from the zero level to level \( m \) as a function of \( X_{\alpha i} \). \( \Delta H_{\alpha i} \) expansion to a power series with respect to \( X_{\alpha} \) gives

\[
\Delta H_{\alpha i} = \sum_{j=0}^{M} \Delta H_{\alpha i j}(X_{\alpha})^j.
\]

(25)

where \( \Delta H_{\alpha ij} \) are the expansion coefficients.

Using equations (17)–(25), we obtain the equation of the molar Gibbs free energy of a mineral with a \( \lambda \)-transition standardized with respect to the ordered state \( (X_{\alpha} = 1) \)

\[
G_{s+\alpha} = G_s + c_{\alpha} G_{\alpha} = H_{T_{e}P_{e}} - TS_{T_{e}P_{e}} + \sum_{i=1}^{n} c_i
\times \{ RT \ln \{ 1 - \exp(-\Delta H_{sia}/RT) \} \}
\times [1 - \exp(-\Delta H_{sia}/RT)]/[ \{1 - \exp(-\Delta H_{sia}/kT)\}
+ \exp(-\Delta H_{sia}/RT)] \exp(-\Delta H_{sia}/RT)
\times \{RT \ln \{1 - \exp(-\Delta H_{sia}/RT)\} - \Delta H_{sia}(1 - T/T_0)\}
\times \exp(-\Delta H_{sia}/RT_0)/[ \{1 - \exp(-\Delta H_{sia}/RT_0)\}
\times \{RT \ln \{1 - \exp(-\Delta H_{sia}/RT_0)\} + V_s^0 \Psi \}
+ c_{\alpha} \{RT[X_{\alpha} \ln(X_{\alpha}) + X_{\beta} \ln(X_{\beta}) + \ldots + X_{D} \ln(X_{D})
+ X_{\alpha} \ln(X_{\alpha}) - \Delta G_{ord}(1 - X_{\alpha})/Z
\]
\]

+ \sum_{j=1}^{M} W_j^0(1 - X_{\alpha})(X_{\alpha})^j \}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
\}
Calculated parameters of equation (28) for coesite and stishovite and equation (30) for quartz

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Quartz</th>
<th>Coesite</th>
<th>Stishovite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{T,P_0}$*</td>
<td>cal/mol</td>
<td>-219329.61**</td>
<td>-218442.65</td>
<td>-209254.14</td>
</tr>
<tr>
<td>$V^0_i$</td>
<td>cal/bar/mol</td>
<td>0.539924</td>
<td>0.490793</td>
<td>0.334656</td>
</tr>
<tr>
<td>$\phi$</td>
<td>bar</td>
<td>71662</td>
<td>217664</td>
<td>612340</td>
</tr>
<tr>
<td>$\Delta V^0$</td>
<td>cal/bar</td>
<td>0.00074714</td>
<td>0.00037909</td>
<td>0.00055788</td>
</tr>
<tr>
<td>$c_1$</td>
<td>cal</td>
<td>1.42569</td>
<td>1.44913</td>
<td>0.28816</td>
</tr>
<tr>
<td>$\Delta H_s$</td>
<td>cal</td>
<td>305.49</td>
<td>343.15</td>
<td>281.81</td>
</tr>
<tr>
<td>$c_2$</td>
<td>cal</td>
<td>3.50283</td>
<td>3.71385</td>
<td>2.73177</td>
</tr>
<tr>
<td>$\Delta H_s$</td>
<td>cal</td>
<td>934.83</td>
<td>979.94</td>
<td>919.28</td>
</tr>
<tr>
<td>$c_3$</td>
<td>cal</td>
<td>4.07148</td>
<td>3.83702</td>
<td>5.98007</td>
</tr>
<tr>
<td>$\Delta H_{ord}$</td>
<td>cal</td>
<td>-630.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta V_{ord}$</td>
<td>cal</td>
<td>-0.030554</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$W^H_i$</td>
<td>cal</td>
<td>3407.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$W^V_i$</td>
<td>cal/bar</td>
<td>0.151422</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta H_{ry}$</td>
<td>cal</td>
<td>3094.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta V_{ry}$</td>
<td>cal/bar</td>
<td>0.057862</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Enthalpy of formation from elements at $T_0 = 0$ K and $P_0 = 1$ bar.
** The value $H_{T,P_0}$ of quartz was taken such that its enthalpy of formation at 298.15 K was $-217678$ cal/mol ($-910.7$ kJ/mol) recommended by CODATA (1978).

derivation of internally consistent thermodynamic data was performed by the nonlinear least squares method. The thermodynamic processing of the experimental data was carried out cyclically with the quality control of reproduced parameters. The calculation procedure allowed us to approximate the measured parameters within experimental errors. For the testing of the equations, the requirement was prescribed of a precise description of the thermodynamic properties of minerals within the wide range of temperature and pressure at $n = 3$ and the empirical values of the weights $c_i$ and parameters $\Delta H^0_{si}$, $\Delta V^0_{si}$ in (18) and $\Delta H^0_{ria}$, $\Delta V^0_{ria}$, $\Delta H^0_{sib}$, $\Delta V^0_{sib}$, $\Delta H^0_{sik}$, and $\Delta V^0_{sik}$ in (26).

The thermodynamic properties of coesite and stishovite were derived using equation (18) with a fixed value of the parameter $\Delta V^0_{si} = \Delta V^0_{s}$ (i.e., independent of $i$). At the chosen $T_0$ and $P_0$ values, the generalized equation for the calculation of the Gibbs free energies of coesite and stishovite is:

$$G_i = H_{T,P_0} + \sum_{i=1}^{3} c_i R T \times \ln \{ 1 - \exp[-(\Delta H^0_{si} + \Delta V^0_{si} \Psi)/RT] \} + V^0_{si} \Psi.$$  

The calculated values of the ten parameters of equation (28) for these minerals are shown in the table.

The processing and modeling of quartz thermodynamic properties in the vicinity of the $\lambda$-transition using equations (19)–(26) demonstrated that the process of its ordering is specified by the intracrystalline reaction

$$3\text{SiO}_2(\text{Qtz}_0) = \text{Si}_3\text{O}_6(\text{Qtz}_a).$$  

This inference agrees with the results obtained for quartz by other researchers (e.g., Castex and Madon, 1995; Spearing et al., 1992). For the simplest mixing
Fig. 1. Variations of the ordering parameter $X_a$ and thermodynamic properties of quartz with temperature and pressure. Calculated by equation (30) with parameters from the table. Numbers on the isolines are pressure in kilobars. (a) Isobars of temperature dependencies of the mole fraction of ordered quartz ($X_a$), (b) Isobars of the temperature dependencies of quartz molar heat capacity. (c) Isobars of the temperature dependencies of quartz molar volume. (d) Negative correlation $r = -0.987$ between the mole fraction of ordered quartz ($X_a$) and the mean square displacement (MSD) of oxygen atoms along axes $I$–$J$ (Kihara, 1990) at $P = 1$ bar and $T = 600$–$1100$ K.
model \([m = 1 \text{ in equation (23)}]\) and \(c_\alpha = 1\), the equation of the Gibbs free energy of quartz is

\[
G_{s,\alpha}(Q_{12}) = H_{s,p} + \sum_{i=1}^{3} c_i R T \times \ln\left\{\frac{[1 - \exp(-\Delta H_{s,\alpha} / R T)]}{[1 - \exp(-\Delta H_{s,\beta} / R T)]} \times \frac{\exp(-\Delta H_{s,\beta} / R T)}{\exp(-\Delta H_{s,\beta} / k T)} + \exp(-\Delta H_{s,\beta} / R T) \right\} + \nu_{s}^0 \Psi + \{ RT[X_{\alpha} \ln(X_{\alpha}) + X_{\beta} \ln(X_{\beta})] - \Delta G_{s,\alpha} / 3 \times (1 + 2 X_{\alpha}) = \min,
\]

where

\[
\Delta H_{s,\alpha} = \Delta H_{s,\alpha}^0 + \Delta V_{s}^0 \Psi,
\]

\[
\Delta H_{s,\beta} = \Delta H_{s,\beta}^0,
\]

\[
\Delta H_{s,\beta} = \Delta H_{s,\beta}^0 X_{\alpha}^2 + \Delta V_{s}^0 \Psi,
\]

\[
W_{1}^G = W_{1}^H + \nu_{s}^0 \Psi,
\]

\[
\Delta G_{s,\alpha} = \Delta H_{s,\alpha}^0 + \Delta V_{s}^0 \Psi,
\]

\[
X_{\alpha} = X_{\beta} = 1,
\]

and \(X_{\alpha}\) is the mole fraction of disordered quartz. The calculated values of all the parameters of equation (30) are shown in the table.

Figure 1a shows variations of \(X_{\alpha}\) with \(T\) and \(P\). It is seen that two equilibrium phases with different proportions of ordered and disordered quartz particles occur along the line of the phase transition. Equilibrium (29) is attained both between the phases and within each of them. The miscibility gap expands with increasing pressure (the calculated critical point of the solvus has a negative pressure value). Below this pressure, only a hypothetical homogenous phase is possible, the ordering parameter of which \(X_{\alpha}\) must change continuously with temperature (Fig. 1a). The heat capacity and thermal expansion coefficient must show maxima at the highest absolute \(\partial X_{\alpha} / \partial T\) values (Figs. 1a, 1b). At pressures above the critical point, the transition between phases is accompanied by a discrete change in \(X_{\alpha}\) (Fig. 1a) and quartz thermodynamic functions (Figs. 1b and 1c). It is known (Hessney et al., 1994) that immediately near the region of phase transition, quartz experiences complex changes of the crystal structure related to the formation of an incommensurate phase. In deriving equation (30), we did not address the problem of the thermodynamic description of this phenomenon, because it occurs in a very narrow temperature range and its physical nature is not completely known. It may be assumed that the energy effect of these transformations in the quartz structure is incorporated in a cumulative form in the parameters \(\Delta H_{s,\alpha}^0\) and \(\Delta V_{s,\alpha}^0\) of equation (30). Figure 1d shows the negative linear correlation of the ordering parameter \(X_{\alpha}\) and the mean square displacement of oxygen atoms in the quartz structure near the \(\lambda\)-transition. The high correlation coefficient \((r = 0.9868)\) demonstrates that the calculated decrease of \(X_{\alpha}\) with increasing temperature (Fig. 1a) directly reflects changes in mutual atom positions in the quartz structure. In other words, the parameter \(X_{\alpha}\) is a precise quantitative characteristic of the degree of ordering for a phase with a \(\lambda\)-transition.

The thermodynamic constants of quartz, coesite, and stishovite presented in the table were obtained on the basis of the following experimental data (Figs. 2–5):

- measurements of low- and high-temperature heat capacity of quartz (Fig. 2a), coesite (Fig. 3a), and stishovite (Fig. 4a);
- volume of quartz (Figs. 2b and 2c), coesite (Figs. 3b and 3c), and stishovite (Figs. 4b and 4c) as functions of temperature and pressure;
- data on the adiabatic compression of quartz (Fig. 2d);
- relative enthalpies of quartz (Fig. 2e) and coesite (Fig. 3d);
- solution enthalpy for the coesite–quartz reaction (Fig. 5a);
- and data on the phase transitions \(\alpha\)-quartz–\(\beta\)-quartz (Fig. 5b), coesite–quartz (Fig. 5c), and coesite–stishovite (Fig. 5d).

During the processing of the data, we used the recommendations of Richet et al. (1992) for the estimation of measurement accuracies.

For the data of adiabatic calorimetry, the following errors were accepted for heat capacity estimates: ±10–20% (below 10 K) and ±0.2% (above 10 K), whereas, for the results of differential scanning calorimetry, ±1% was accepted below 1000 K and ±5% above 1000 K.

The accuracy of the initial data for the measurement of relative enthalpy by the method of mixing calorimetry was estimated as ±1%.

The comparison of results of volume measurements for silica polymorphs from various sources allowed us to estimate the accuracy of the unit-cell volumes of quartz, coesite, and stishovite within the whole temperature and pressure interval as ±0.3%. The large error is due to a considerable scatter of measurements from various experimental series. For example, the measurements of quartz molar volume at standard state conditions \((T = 298 K \text{ and } P = 1 \text{ atm})\) range from 22.63 cm\(^3\) (Burnham, 1965) to 22.81 cm\(^3\) (Glimnemann et al., 1992); coesite molar volume, from 20.50 cm\(^3\) (Bassett and Barnett, 1970) to 20.67 cm\(^3\) (Robie et al., 1967); and stishovite molar volume, from 13.99 cm\(^3\) (Bassett and Barnett, 1970) to 14.05 cm\(^3\) (Liu et al., 1974; Endo et al., 1986).
Fig. 2. Comparison of the calculated values of quartz thermodynamic properties with experimental data. Calculated by equation (30) with parameters from the table.

(a) Heat capacity at constant pressure. Calorimetric data after (1) Hemingway et al., 1991; (2) Gurevich and Khlyustov, 1979; (3) Watanabe, 1982; (4) Gronvold et al., 1989; (5) Akaogi et al., 1995; (6) Hemingway, 1987; and (7) calculated parameters using data from the table.

(b) Temperature dependence of molar volume. (1) Calculated using data from the table; (2) Jay, 1933; (3) Ackermann and Sorell, 1974; (4) Danielsson et al., 1976; (5) Lager et al., 1982; (6) Kihara, 1990; and (7) Carpenter et al., 1998.

(c) Pressure dependence of molar volume. (1) Calculated using data from the table; (2) Vaidya et al., 1973; (3) Olinger and Hale, 1974; (4) Jorgensen, 1978; (5) d’Amour et al., 1979; (6) Levien et al., 1980; (7) Hazen et al., 1989; and (8) Glinsmann et al., 1992.

(d) Adiabatic compression. (1) Calculated using parameters from the table; (2) 298, (3) 800, (4) 1000, and (5) 1300 K (Boehler et al., 1979; Boehler, 1982).

(e) Relative molar enthalpy. (1) Calculated using data from the table and (2) (Richet et al., 1982).
Fig. 3. Comparison of the calculated values of the coesite thermodynamic properties with experimental data. Calculated by equation (28) using parameters from the table.
(a) Heat capacity at constant pressure. (1) Calculated using data from the table; (2) (Holme et al., 1967); and (3) (Akaogi et al., 1995).
(b) Temperature dependence of molar volume. (1) Calculated using data from the table; (2) (Galkin et al., 1987); and (3) (Smyth et al., 1987). Bars show errors in volume determination of ±0.3%.
(c) Pressure dependence of molar volume. (1) Calculated using data from the table; (2) (Bassett and Barnett, 1970); and (3) (Levien and Prewitt, 1981). Bars show errors in volume and pressure determinations of ±0.3 and ±5%, respectively.
(d) Relative molar enthalpy. (1) Calculated using data from the table; (2) (Holme et al., 1967); (3) (Akaogi and Navrotsky, 1984); and (4) (Akaogi et al., 1995).
Fig. 4. Comparison of the calculated values of the stishovite thermodynamic properties with experimental data. Calculated by equation (28) using parameter from the table. 
(a) Heat capacity at constant pressure. (1) Calculated using data from the table; (2) (Holm et al., 1967); and (3) (Akaogi et al., 1995). (b) Temperature dependence of molar volume. (1) Calculated using data from the table at $P = 1$ bar; (2) calculated using data from the table at 105 kbar; (3) (Doroshev et al., 1987, 1 bar); (4) (Endo et al., 1986, 1 bar); and (5) (Suito et al., 1996, 105 kbar). Bars show errors in volume determinations of ±0.3%. (c) Pressure dependence of molar volume. (1) Calculated using data from the table; (2) (Bassett and Barnett, 1970); (3) (Liu et al., 1974); (4) (Olinger, 1976); (5) (Sato, 1977); (6) (Tsuchida and Yagi, 1989); (7) (Ross et al., 1990); and (8) (Suito et al., 1996).
The accuracy of pressure determination was taken to be no better than ±5%. For all other measured parameters, the accuracy, given by the authors, was accepted.

In Figs. 2–5, the calculating results using equations (28) and (29) are compared with the initial data. It is evident that our thermodynamic formalism correctly reproduces the experimental relationships.

The extrapolation characteristics of the model were checked by application to the experimental data that were not involved in the processing. Figure 4c demonstrates good agreement between the stishovite volume...

CONCLUSION

ON THE BASIS OF THE T--P PARTITION FUNCTION, THE LANDAU THEORY OF PHASE TRANSITIONS, AND THERMODYNAMICS OF SOLID SOLUTIONS AN EQUATION OF STATE WAS DERIVED FOR MINERALS. IT IS BASED ON THE PRINCIPLE OF THE MINIMUM OF THE GIBBS FREE ENERGY IN THE EQUILIBRIUM STATE OF A CRYSTALLINE PHASE AT GIVEN TEMPERATURE AND PRESSURE. THE EQUATION OF STATE ALLOWS DESCRIPTION OF THE THERMODYNAMIC PROPERTIES OF MINERALS WITHIN EXPERIMENTAL ERROR AND SHOWS GOOD EXTRAPOLATION CHARACTERISTICS. TOGETHER WITH THE SIMILAR EQUATION OF STATE FOR DENSE GASES (GERYA AND PERCHUK, 1997) EQUATIONS (18), (26), AND (27) MAY BE USED AS A BASIS FOR THE DEVELOPMENT OF INTERNALLY CONSISTENT THERMODYNAMIC DATABASES FOR USE IN PETROLOGY.

ACKNOWLEDGMENTS


REFERENCES


BASSETT, W.A. AND BARNETT, J.D., ISOTHERMAL COMPRESSION OF STISHOVITE AND COESITE UP TO 85 KILOBARS AT ROOM TEMPERATURE BY X-RAY DIFFRACTION, PHYS. EARTH PLANET. INTER., 1970, VOL. 3, PP. 54--60.


