Equation of State of Minerals for Thermodynamic Databases Used in Petrology

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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 λ-transition, the Gibbs free energy is defined as a function of temperature (T), pressure (P), and ordering parameter (X_a). The equilibrium mole fraction of ordered particles (X_a) is determined from the condition $G = f(P, T, X_a) = \text{min}$. Application to the system coesite–stishovite–α-quartz–β-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 Kuskov, 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 Kuskov, 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 Kuskov, 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; Saxena *et al.*, 1993) use the standard expression of the molar Gibbs free energy in the form:

$$\Delta G(P, T) = \Delta H_o - TS_o + \int_{T_0}^{T} [C_{Po}(T)]dT$$

$$- T\int_{T_0}^{T} [C_{Po}(T)/T]dT + \int_{P_0}^{P} [V(P, T)]dP,$$

(1)

where P is pressure; T is temperature; $G(T, P)$ is the molar Gibbs free energy at given P and T; ΔH_o and S_o are the enthalpy of formation and entropy, respectively, of the matter at reference temperature T_0 and pressure P_0; $C_{Po}(T)$ is the heat capacity as a function of temper-

ature at reference pressure P_0; and $V(P, T)$ is the volume of the substance as a function of temperature and pressure. The form of the functions $C_{Po}(T)$ and $V(P, T)$ is selected empirically; power expansion series are normally used and allow the approximation of experimental data on phase equilibria and (or) thermochemical measurements for a number of minerals with a reasonable degree of accuracy.

In many cases, the application of thermodynamic databases (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, η. The equilibrium value of η at P and T corresponds to the minimum of the Gibbs free energy:

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

where η 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):

$$G = -kT\ln(Y), \qquad (2)$$

where

$$Y = \sum_i \int_0^\infty \exp\{-[E_i(V) + PV]/kT\}dV, \qquad (3)$$

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 ith 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 ith quantum state at a given P, there is a unique value of the system volume $V_i(P)$ with the non-zero probability, then

$$\int_0^\infty \exp\{-[E_i(V) + PV]/kT\}dV = \exp[-H_i(P)/kT], (4)$$

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 ith 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 ith 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

$$Y = \sum_i \exp[-H_i(P)/kT]. \qquad (5)$$

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

$$G = G_0(P) - kT\ln(Y_0), \qquad (6)$$

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 sate 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 ith 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:

$$Y_0 = \prod_i^{3N} Y_{0i}, \qquad (7)$$

where

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

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

Y_{0i} is the statistical sum for the ith oscillator normalized with respect to the state of zero-point vibrations; M is the number of energy levels for the ith 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 ith oscillator from the state of zero-point vibrations into the jth 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-

ues $\Delta H_{ij}(P)$, $\Delta E_{ij}(P)$, and $\Delta V_{ij}(P)$ are proportional to the level index (j). In this case,

$$\Delta H_{ij}(P) = j\Delta H_{i0}(P), \qquad (8)$$

$$Y_{0i} = 1/\{1 - \exp[-\Delta H_{i0}(P)/kT]\}, \qquad (9)$$

where

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

$\Delta H_{i0}(P)$, $\Delta E_{i0}(P)$, and $\Delta V_{i0}(P)$ are enthalpy, energy, and volume effects due to transition of the ith 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

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

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

$$G_S = H_S - TS_S^0$$
$$+ RT\sum_i^n c_i\ln\{1 - \exp[-\Delta H_{si}/RT]\}, \qquad (11)$$

where

$$R = kN_A,$$

$$c_i = N_i/N_A, \quad \sum_i^n c_i = 3\nu,$$

$$\Delta H_{si} = N_A\Delta H_{i0},$$

$R = 1.987$ cal/mol/K; H_S 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 ΔH_{i0}; H_i is the number of oscillators in the ith group; c_i is the statistical weight of the ith group; ΔH_{si} is the enthalpy effect of the transition between neighboring energy levels for the ith group (calculated for N_A oscillators).

The application of equation (11) requires incorporation of pressure dependencies of H_S and ΔH_{Si}. This can be made using the expressions

$$H_s = H_s^0 + \int_{P_0}^P V_s dP, \qquad (12)$$

$$\Delta H_{si} = \Delta H_{si}^0 + \int_{P_0}^P \Delta V_{si} dP, \qquad (13)$$

where P_0 is the reference pressure; H_s^0 is the molar enthalpy of the solid at 0 K and P_0; ΔH_{si}^0 is the value of ΔH_{si} at P_0; V_s is the molar volume of the solid at 0 K as a function of pressure; and ΔV_{si} is the volume effect of the transition between neighboring energy levels for the ith 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,

$$V_S = V_S^0(P_0 + \phi)^{1/5}/(P + \phi)^{1/5}, \qquad (14)$$

where V_S^0 is the molar volume at 0 K and P_0; ϕ 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 ΔV_{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 ith group. Expressing this change as an apparent small increment to V_s similar to (14) gives

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

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

$$H_s = H_s^0 + V_s^0\Psi, \qquad (16)$$

$$\Delta H_{si} = \Delta H_{si}^0 + \Delta V_{si}^0\Psi, \qquad (17)$$

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

$$G_s = H_{T_0 P_0} - T S_{T_0 P_0}$$

$$+ \sum_{i=1}^{n} c_i \{ RT \ln[1 - \exp(-\Delta H_{si}/RT)]$$

$$- \Delta H_{si}^0 (1 - T/T_0) \exp(-\Delta H_{si}^0/RT_0)/[1$$

$$- \exp(-\Delta H_{si}^0/RT_0)] - RT \ln[1$$

$$- \exp(-\Delta H_{si}^0/RT_0)] \} + V_s^0 \Psi,$$

(18)

where

$$S_{T_0 P_0} = -(\partial G_s/\partial T)_{T_0 P_0} = S_s^0 + \sum_i^n c_i$$

$$\times \{ \Delta H_{si}^0/T_0 \exp(-\Delta H_{si}^0/RT_0)/[1$$

$$- \exp(-\Delta H_{si}^0/RT_0)]$$

$$- R \ln[1 - \exp(-\Delta H_{si}^0/RT_0)] \},$$

$$H_{T_0 P_0} = G_{T_0 P_0} + T_0 S_{T_0 P_0} = H_s^0 + \sum_i^n c_i \Delta H_{si}^0$$

$$\times \exp(-\Delta H_{si}^0/RT_0)/[1 - \exp(-\Delta H_{si}^0/RT_0)],$$

$$G_{T_0 P_0} = H_s^0 - T_0 S_s^0 + RT_0 \sum_i^n c_i$$

$$\times \ln\{1 - \exp[-\Delta H_{si}^0/RT_0]\} = H_{T_0 P_0} - T_0 S_{T_0 P_0},$$

and $G_{T_0 P_0}$, $H_{T_0 P_0}$, and $S_{T_0 P_0}$ 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, ΔH_{si}^0, and ΔV_{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, ΔH_{si}^0, and ΔV_{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 λ-transition, the dependency on the ordering parameter η must be incorporated into equation (18). This will be made by the thermodynamic analysis of the ordering process in the most general form

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

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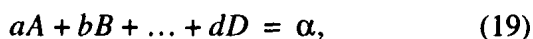
where A, B, ..., D are disordered particles; $\alpha = A_a B_b \dots D_d$ is the ordered particle, and $a, b, \dots, d$ are the stoichiometric coefficients. The condition of intracrystalline equilibrium for reaction (19) is given by

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

(20)

where

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

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

X_A, X_B, ..., X_D are the mole fractions of the disordered particles A, B, ..., D, respectively; X_α is the mole fraction of the ordered particle α; K_{ord} is in principle similar to the equilibrium constant of a chemical reaction similar to (19); ΔG_{ord}^0 and ΔG_{ord}^e 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

$$G_\alpha = \{ RT[X_A \ln X_A + X_B \ln(X_B) + \dots + X_D \ln(X_D)$$

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

(21)

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

where $Z = a + b + \dots + d$ is the normalizing factor; G_{ord}^e 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

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

(22)

where $G_{s+\alpha}$ is the molar Gibbs free energy of a mineral with a λ-transition; c_α 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

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

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

(23)

where

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

$$\Delta G_{ord}^0 = \Delta H_{ord}^0 + \Delta V_{ord}^0 \Psi,$$

ΔH_{ord}^0 and ΔV_{ord}^0 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_α, there is a change in the volume and enthalpy effects of

transitions between neighboring energy levels. The statistical sums Y_{0i} in (7) become

$$Y_{0i} = 1/\{[1 - \exp(-\Delta H_{i\alpha}/kT)]$$

$$\times [1 - \exp(-\Delta H_{i\beta}/kT)]/\{[1 - \exp(-\Delta H_{i\beta}/kT)]$$

$$+ \exp(-\Delta H_{i\lambda}/kT)[\exp(-\Delta H_{i\beta}/kT) \qquad (24)$$

$$- \exp(-\Delta H_{i\alpha}/kT)]\}\},$$

where $\Delta H_{i\alpha}$ is the enthalpy effect of energy transitions (ΔH_{i0}) from the zero level to level $(m - 1)$ typical of the ordered phase; $\Delta H_{i\beta}$ is the enthalpy effect of energy transitions (ΔH_{i0}) from level m typical of the disordered phase; $\Delta H_{i\lambda}$ is the enthalpy effect of transition from the zero level to level m as a function of X_α. $\Delta H_{i\lambda}$ expansion to a power series with respect to X_α gives

$$\Delta H_{i\lambda} = \sum_{j=0}^{M} \Delta H_{i\lambda j}(X_\alpha)^j, \qquad (25)$$

where $\Delta H_{i\lambda j}$ are the expansion coefficients.

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

$$G_{s+\alpha} = G_s + c_\alpha G_\alpha = H_{T_0 P_0} - TS_{T_0 P_0} + \sum_{i=1}^{n} c_i$$

$$\times \{RT\ln\{[1 - \exp(-\Delta H_{si\alpha}/RT)]$$

$$\times [1 - \exp(-\Delta H_{si\beta}/RT)]/\{[1 - \exp(-\Delta H_{si\beta}/kT)]$$

$$+ \exp(-\Delta H_{si\lambda}/RT)[\exp(-\Delta H_{si\beta}/RT)$$

$$- \exp(-\Delta H_{si\alpha}/RT)]\}\} - \Delta H_{si\alpha}^0(1 - T/T_0)$$

$$\times \exp(-\Delta H_{si\alpha}^0/RT_0)/[1 - \exp(-\Delta H_{si\alpha}^0/RT_0)] \qquad (26)$$

$$- RT\ln[1 - \exp(-\Delta H_{si\alpha}^0/RT_0)]\} + V_s^0\Psi$$

$$+ c_\alpha\left\{RT[X_A\ln(X_A) + X_B\ln(X_B) + \dots + X_D\ln(X_D)\right.$$

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

$$+ \sum_{j=1}^{m} W_j^G(1 - X_\alpha)(X_\alpha)^j\left.\right\}/[1 + X_\alpha(Z - 1)] = \min,$$

where

$$\Delta H_{si\alpha} = \Delta H_{si\alpha}^0 + \Delta V_{si\alpha}^0\Psi,$$

$$\Delta H_{si\beta} = \Delta H_{si\beta}^0 + \Delta V_{si\beta}^0\Psi,$$

$$\Delta H_{si\lambda} = \sum_{j=0}^{M}(\Delta H_{si\lambda j}^0 + \Delta V_{si\lambda j}^0\Psi)(X_\alpha)^j$$

and $\Delta H_{si\alpha}$, $\Delta H_{si\beta}$, and $\Delta H_{si\lambda j}$ are the values of $\Delta H_{i\alpha}$, $\Delta H_{i\beta}$, and $\Delta H_{i\lambda j}$ calculated for N_A oscillators. The meaning of all the other parameters in (26) is evident from the derivation of the previous equations.

If the heat expansion coefficient does not change at the λ-transition, equation (26) taking into account (18) becomes

$$G_{s+\alpha} = G_s + c_\alpha G_\alpha = H_{T_0 P_0} - TS_{T_0 P_0} + \sum_{i=1}^{n} c_i$$

$$\times \{RT\ln[1 - \exp(-\Delta H_{si}/RT)] - \Delta H_{si}^0(1 - T/T_0)$$

$$\times \exp(-\Delta H_{si}^0/RT_0)/[1 - \exp(-\Delta H_{si}^0/RT_0)]$$

$$- RT\ln[1 - \exp(-\Delta H_{si}^0/RT_0)]\} + V_s^0\Psi \qquad (27)$$

$$+ c_\alpha\left\{RT[X_A\ln(X_A) + X_B\ln(X_B) + \dots + X_D\ln(X_D)\right.$$

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

$$+ \sum_{j=1}^{M} W_j^G(1 - X_\alpha)(X_\alpha)^j\left.\right\}/[1 + X_\alpha(Z - 1)] = \min,$$

where $\Delta H_{si} = \Delta H_{si}^0 + \Delta V_{si}^0\Psi$.

Expressions (26) and (27) are *equations of the Gibbs free energy of a mineral with a λ-transition* as a function of P, T, and X_α. To calculate the thermodynamic properties of the mineral, the equilibrium value of X_α should be found from equation (20) corresponding to the minimum of Gibbs free energy in (26) or (27). The expression for the calculation of changes in the standard and excess Gibbs free energies in equation (20) may be obtained from equations (26) or (27) using the Gibbs–Duhem relation.

Equations (18) and (26) or (27) are the desired equations of state. They may be used to calculate internally consistent thermodynamic constants and create thermodynamic databases.

TESTING

The efficiency of the derived equations was analyzed with the system coesite–stishovite–α-quartz–β-quartz, which was often used as a test system for various equations of state (Kuskov and Fabrichnaya, 1987; Swamy *et al.*, 1994; Dorogokupets, 1995). The standard state conditions were $T_0 = 0$ K and $P_0 = 1$ bar. Such a choice allowed us to simplify equations (18) and (26) and to check the accuracy of the representation of experimental data in a low-temperature region (0–298 K). The

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Calculated parameters of equation (28) for coesite and stishovite and equation (30) for quartz

Parameter	Units	Quartz	Coesite	Stishovite
$H_{T_0 P_0}$*	cal/mol	-219329.61**	-218442.65	-209254.14
V_s°	cal/bar/mol	0.539924	0.490793	0.334656
ϕ	bar	71662	217664	612340
ΔV_s°	cal/bar	0.00074714	0.00037909	0.00055788
c_1		1.42569	1.44913	0.28816
ΔH_{s1}	cal	305.49	343.15	281.81
c_2		3.50283	3.71385	2.73177
ΔH_{s2}	cal	934.83	979.94	919.28
c_3		4.07148	3.83702	5.98007
ΔH_{s3}	cal	2502.38	2504.76	1922.40
ΔH_{ord}°	cal	-630.28		
ΔV_{ord}°	cal/bar	-0.030554		
W^{H_1}	cal	3407.29		
W^{V_1}	cal/bar	0.151422		
$\Delta H_{s\gamma}^\circ$	cal	3094.80		
$\Delta V_{s\gamma}^\circ$	cal/bar	0.057862		

* Enthalpy of formation from elements at $T_0 = 0$ K and $P_0 = 1$ bar.

** The value $H_{T_0 P_0}$ of quartz was taken such that its enthalpy of formation at 298.15 K was -217678 cal/mol (-910.7 kJ/mol) re-commended 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 ΔH_{si}^0, ΔV_{si}^0 in (18) and $\Delta H_{si\alpha}^0$, $\Delta V_{si\alpha}^0$, $\Delta H_{si\beta}^0$, $\Delta V_{si\beta}^0$, $\Delta H_{si\lambda j}^0$, and $\Delta V_{si\lambda j}^0$ in (26).

The thermodynamic properties of coesite and stishovite were derived using equation (18) with a fixed value of the parameter $\Delta V_{si}^0 = \Delta V_s^0$ (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:

$$G_s = H_{T_0 P_0} + \sum_{i=1}^{3} c_i RT$$

$$\times \ln\{1 - \exp[-(\Delta H_{si}^0 + \Delta V_s^0 \Psi)/RT]\} + V_s^0 \Psi. \quad (28)$$

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 λ-transition using equations (19)–(26) demonstrated that the process of its ordering is specified by the intracrystalline reaction

$$3SiO_2(Qtz_\beta) = Si_3O_6(Qtz_\alpha). \quad (29)$$
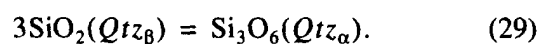
This inference agrees with the results obtained for quartz by other researchers (e.g., Castex and Madon, 1995; Spearing *et al.*, 1992). For the simplest mixing
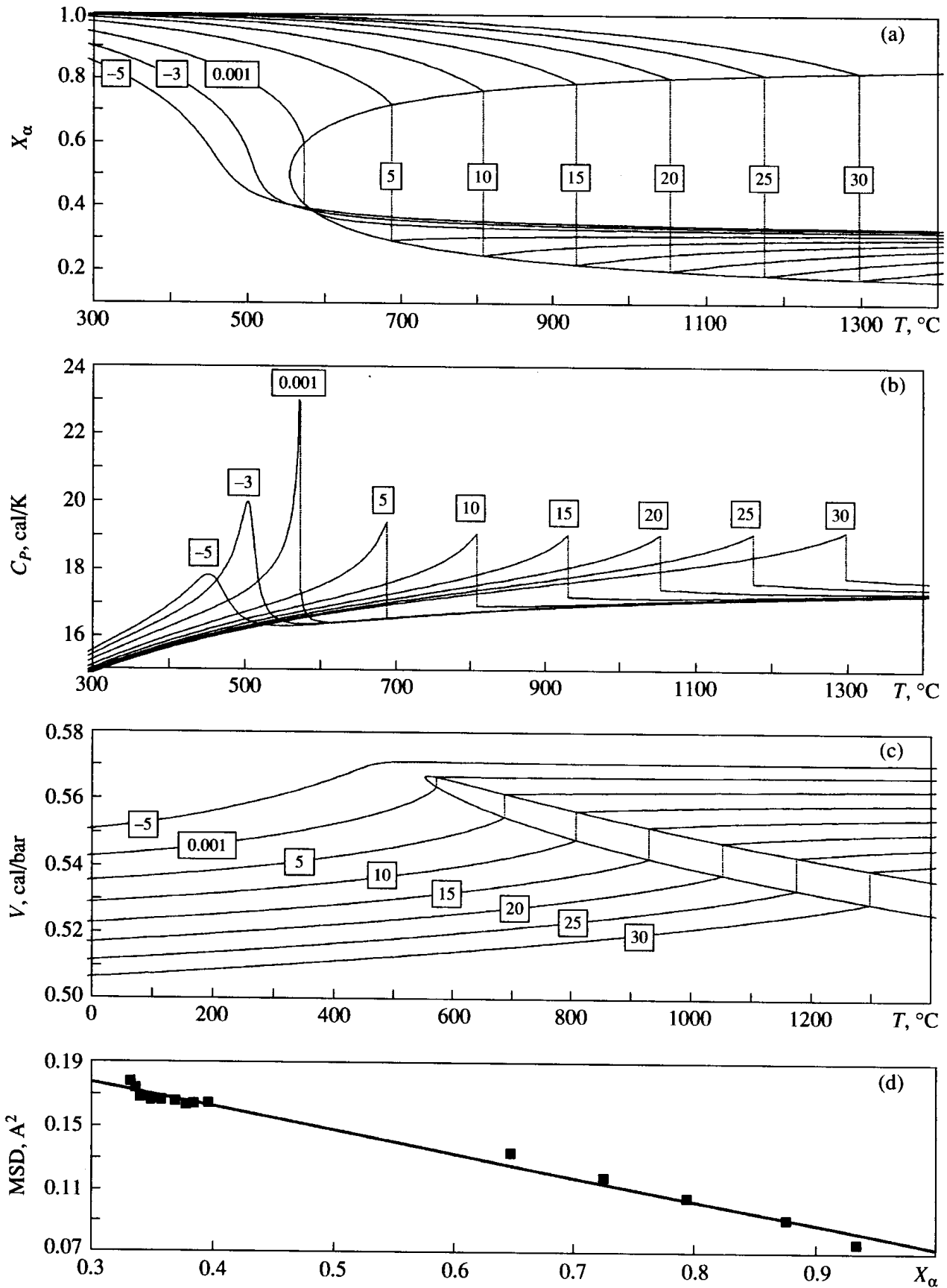
Fig. 1. Variations of the ordering parameter X_α and thermodynamic properties of quartz with temperature and pressure. Calculated by equation (30) with parameters from the table. Numbers on the isolines are pressure in kilobars.

(a) Isobars of temperature dependencies of the mole fraction of ordered quartz (X_α). (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_α) and the mean square displacement (MSD) of oxygen atoms along axes *1–3* (Kihara, 1990) at $P = 1$ bar and $T = 600$–1100 K.

model [$m = 1$ in equation (23)] and $c_\alpha = 1$, the equation of the Gibbs free energy of *quartz* is

$$G_{s+\alpha}(Qtz) = H_{T_0 P_0} + \sum_{i=1}^{3} c_i RT$$

$$\times \ln\{[1 - \exp(-\Delta H_{si\alpha}/RT)]$$

$$\times [1 - \exp(-\Delta H_{si\beta}/RT)]/\{[1 - \exp(-\Delta H_{si\beta}/kT)]$$

$$+ \exp(-\Delta H_{s\lambda}/RT)[\exp(-\Delta H_{si\beta}/RT) \qquad (30)$$

$$- \exp(-\Delta H_{si\alpha}/RT)]\}\} + V_s^0 \Psi$$

$$+ \{RT[X_\alpha \ln(X_\alpha) + X_\beta \ln(X_\beta)] - \Delta G_{ord}^0(1 - X_\alpha)/3$$

$$+ W_1^G X_\beta X_\alpha\}/(1 + 2X_\alpha) = \min,$$

where

$$\Delta H_{si\alpha} = \Delta H_{si}^0 + \Delta V_s^0 \Psi,$$

$$\Delta H_{si\beta} = \Delta H_{si}^0,$$

$$\Delta H_{s\lambda} = \Delta H_{s\lambda}^0 X_\alpha^2 + \Delta V_{s\lambda}^0 \Psi,$$

$$W_1^G = W_1^H + W_1^V \Psi,$$

$$\Delta G_{ord}^0 = \Delta H_{ord}^0 + \Delta V_{ord}^0 \Psi,$$

$$X_\alpha + X_\beta = 1,$$

and X_β 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_α 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_α 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_α (Fig. 1a) and quartz thermodynamic functions (Figs. 1b and 1c). It is known (Heaney *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 transforma-

tions in the quartz structure is incorporated in a cumulative form in the parameters ΔH_{ord}^0 and ΔV_{ord}^0 of equation (30). Figure 1d shows the negative linear correlation of the ordering parameter X_α and the mean square displacement of oxygen atoms in the quartz structure near the λ-transition. The high correlation coefficient ($r = 0.9868$) demonstrates that the calculated decrease of X_α with increasing temperature (Fig. 1a) directly reflects changes in mutual atom positions in the quartz structure. In other words, the parameter X_α is a precise quantitative characteristic of the degree of ordering for a phase with a λ-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 α-quartz–β-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 and $P = 1$ atm) range from 22.63 cm³ (Burnham, 1965) to 22.81 cm³ (Glinnemann *et al.*, 1992); coesite molar volume, from 20.50 cm³ (Bassett and Barnett, 1970) to 20.67 cm³ (Robie *et al.*, 1967); and stishivite molar volume, from 13.99 cm³ (Bassett and Barnett, 1970) to 14.05 cm³ (Liu *et al.*, 1974; Endo *et al.*, 1986).
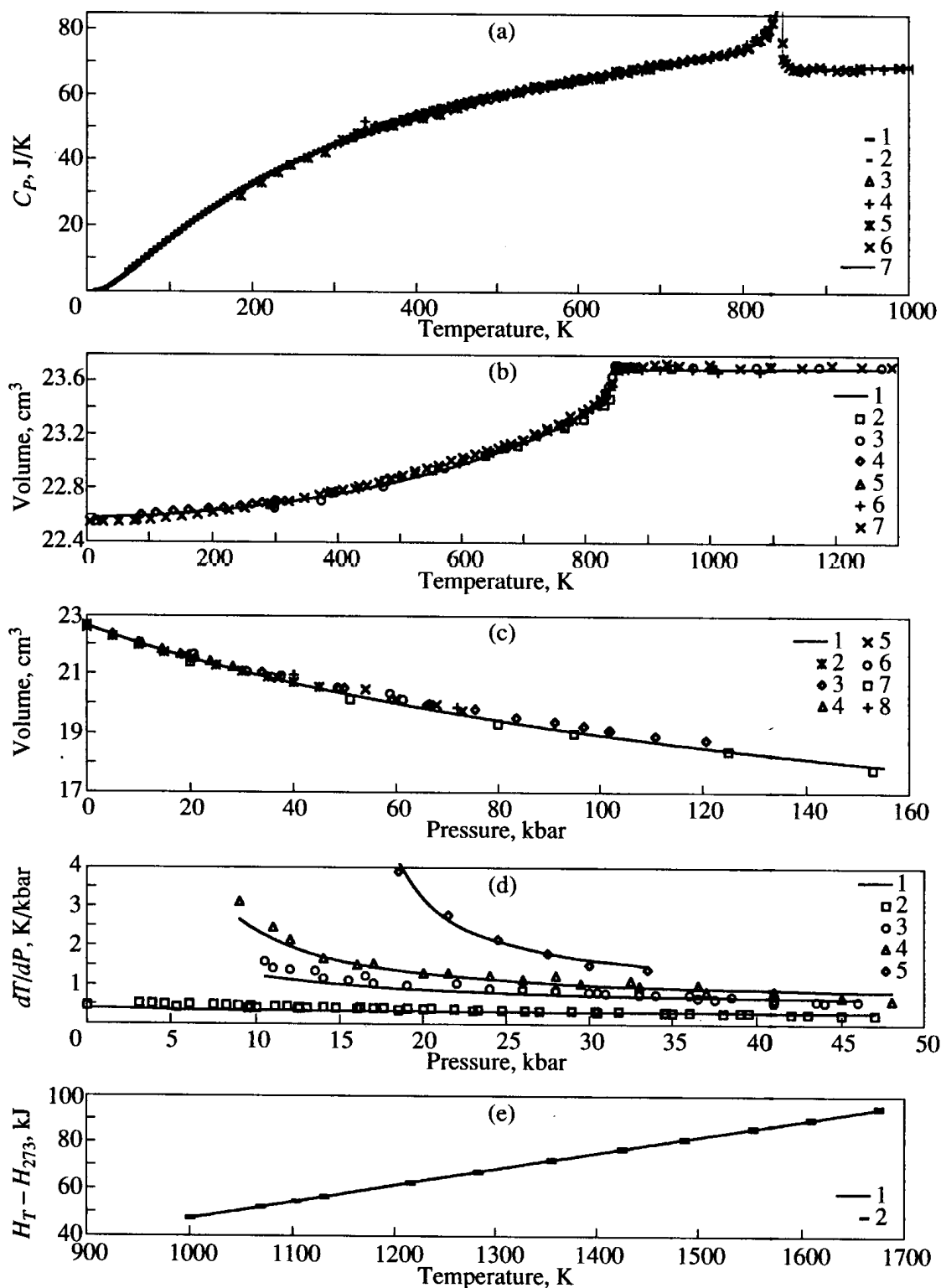
Fig. 2. Comparison of the calculated values of quartz thermodynamic properties with experimental data. Calculated by equation (30) with parameters from the table.
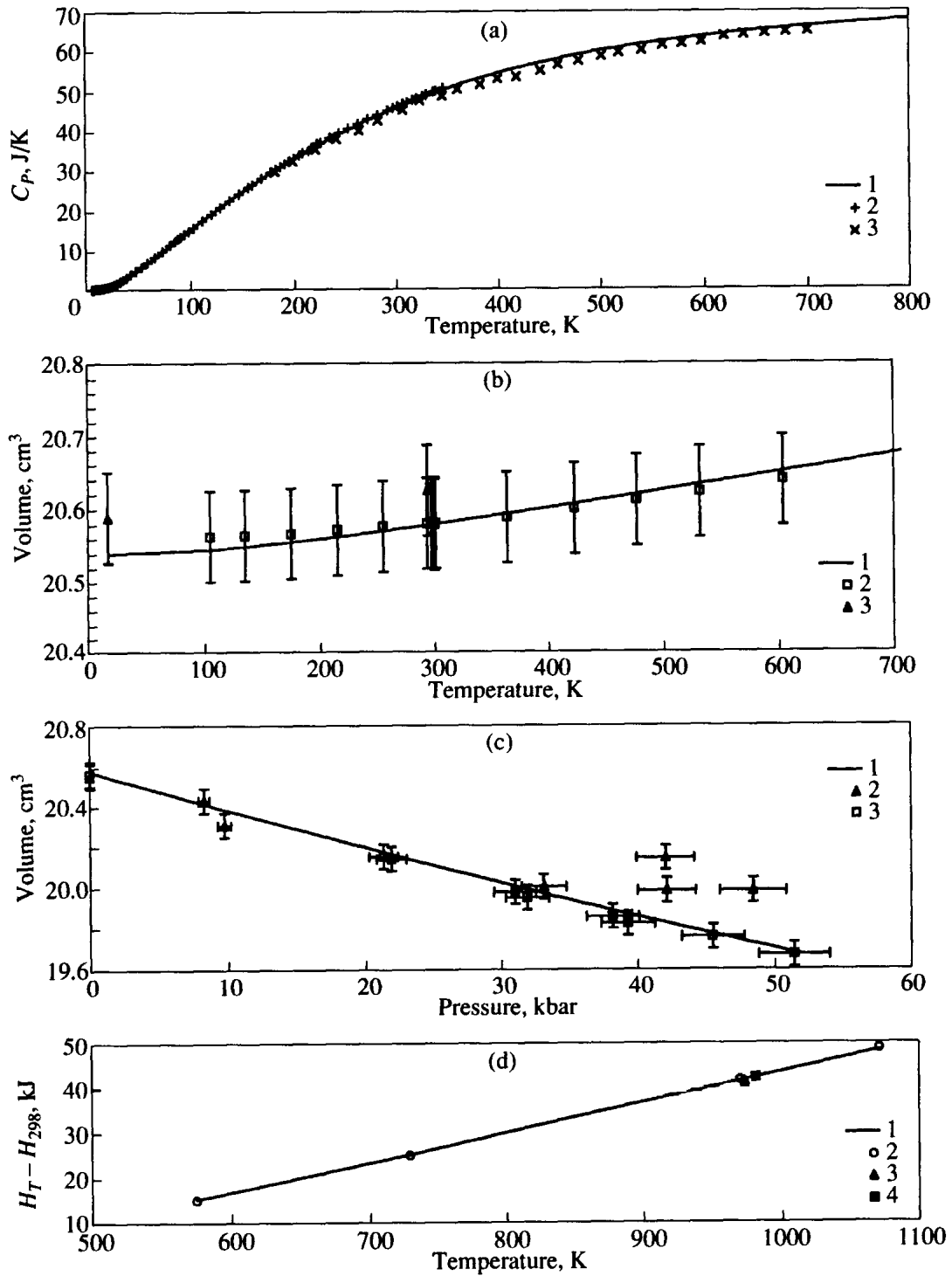
(a) Heat capacity at constant pressure. Calorimetric data after (1) (Hemingway *et al.*, 1991); (2) (Gurevich and Khlyustov, 1979); (3) (Watanabe, 1982); (4) (Gronvold *et al.*, 1989); (5) (Akaogi *et al.*, 1995); (6) (Hemingway, 1987); and (7) calculated parameters using data from the table.

(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 Halleck, 1974); (4) (Jorgensen, 1978); (5) (d'Amour *et al.*, 1979); (6) (Levien *et al.*, 1980); (7) (Hazen *et al.*, 1989); and (8) (Glinnemann *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) (Holm *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) (Holm *et al.*, 1967); (3) (Akaogi and Navrotsky, 1984); and (4) (Akaogi *et al.*, 1995).
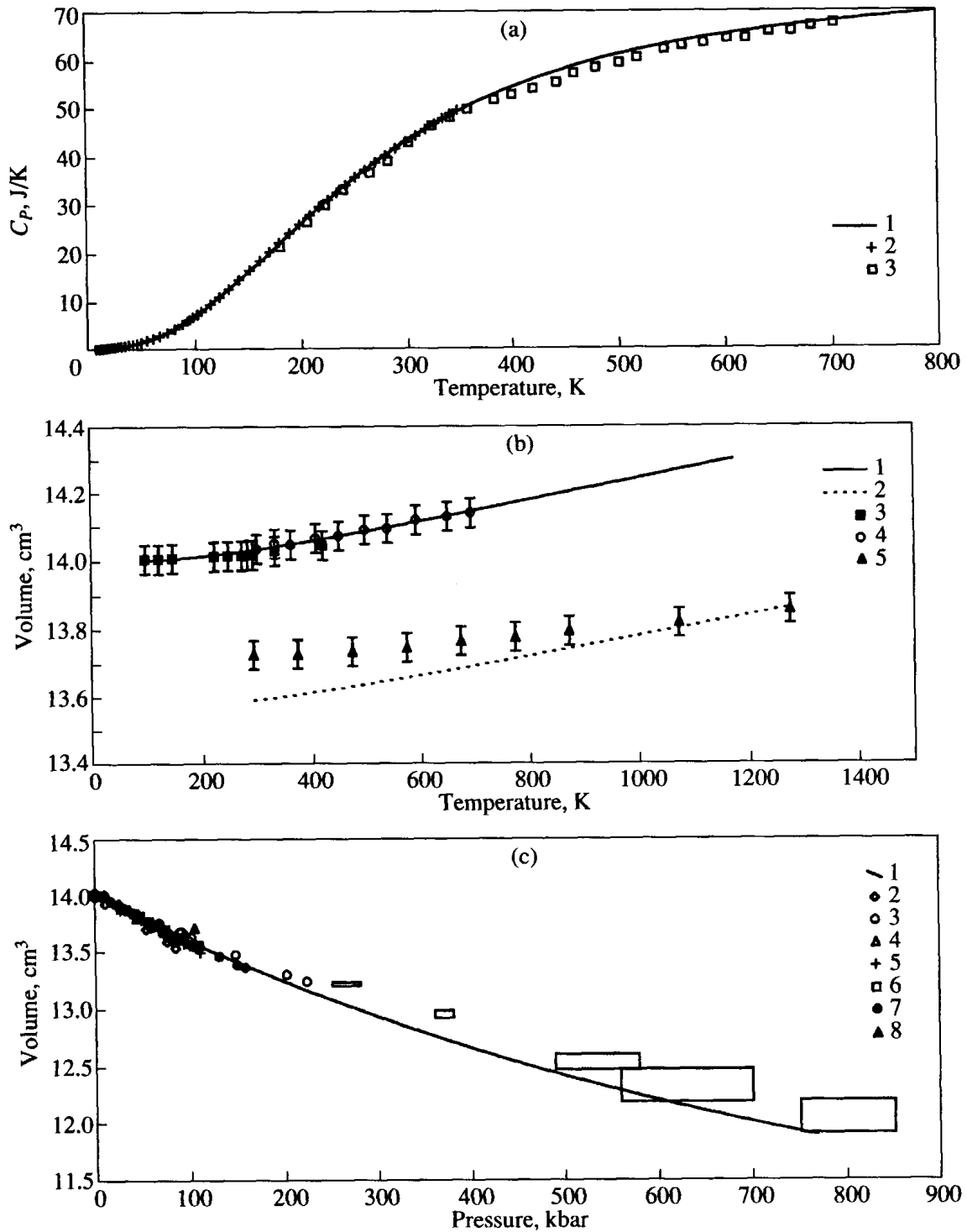
Fig. 4. Comparison of the calculated values of the stishovite thermodynamic properties with experimental data.

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).
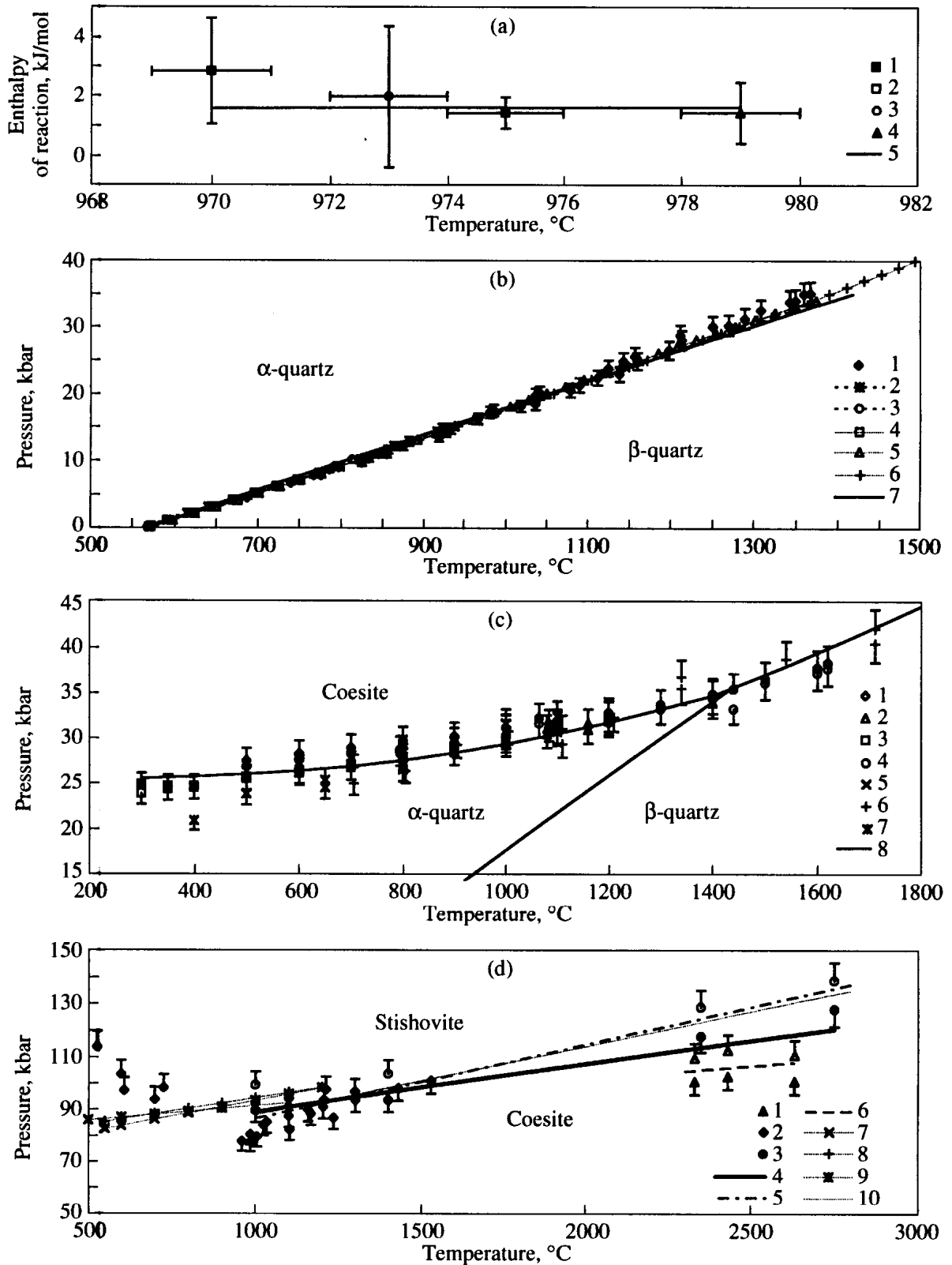
The accuracy of *pressure* determination was taken to be no better than ±5%. For all other measured parameters, the accuracy given by the authors was accepted.

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

Fig. 5. Comparison of the calculated parameters of the phase transitions in the system coesite–stishovite–α-quartz–β-quartz with experimental data. Calculated by equations (28) and (30) using parameters from the table.

(a) Enthalpy of the quartz–coesite phase transition. (1–4) Calorimetric data (error bars show scatter in enthalpy measurements and temperature errors of ±1°C): (1) (Holm *et al.*, 1967); (2) (Akaogi and Navrotsky, 1984); (3) (Kuskov *et al.*, 1991); (4) (Akaogi *et al.*, 1995); and (5) calculated using data from the table.

(b) Phase transition α-quartz–β-quartz. (1) Experimental data (Cohen and Klement, 1967) with error bars for pressure determinations of ±5%. (2–7) Results of processing of the experimental data: (2) (Gibson, 1928); (3) (Yoder, 1950); (4) (Koster van Groos and Ten Heege, 1978); (5) (Mirwald and Massone, 1980b); (6) (Shen *et al.*, 1993); and (7) calculated using parameters from the table.

(c) Phase transition quartz–coesite. (1–8) Experimental data (filled symbols show coesite stable, open symbols, quartz stable; also shown are pressure errors of ±5% and reversed equilibria): (1) (Bose and Ganguly, 1995); (2) (Ishbulatov and Kosyakov, 1990); (3) (Bohlen and Boettcher, 1982); (4) (Mirwald and Massone, 1980a, 1980b); (5) (Akella, 1979) corrected by Mirwald and Massone (1980a); (6) (Boyd and England, 1960), nominal pressure corrected using the equation of Gasparik and Newton (1984) for the temperature dependency of friction correction; (7) (Kitihara and Kennedy, 1964); and (8) calculated using parameters from the table.

(d) Coesite–stishovite phase transition. (1–3) Experimental data (solid symbols show coesite stable, open symbols, stishovite stable; also shown are error bars for pressure determination of ±5% and reversal experiments): (1) (Serghiou *et al.*, 1995); (2) (Zhang *et al.*, 1996); (3) (Zhang *et al.*, 1993). (4–10) Results of the processing of the experimental data: (4) calculated using parameters from the table; (5) (Zhang *et al.*, 1993); (6) (Seghiou *et al.*, 1995); (7) (Akimoto and Syono, 1969); (8) (Suito, 1977); (9) (Yagi and Akimoto, 1976); and (10) (Zhang *et al.*, 1996).

extrapolated using equation (28) to a pressure of 800 kb and independent experimental data (Tsuchida and Yagi, 1989). The calculated temperature dependency of quartz volume (Fig. 2b) is also quite consistent with recent independent determinations (Carpenter *et al.*, 1998).

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

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