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Semi-empirical Gibbs free energy formulations for minerals and fluids for use in thermodynamic databases of petrological interest

Abstract The P–T partition function in statistical thermodynamics can be used to derive semi-empirical formulations of the Gibbs free energy G for minerals and fluids. Parameterization of these equations includes simultaneous regression of experimental heat capacity and molar volume data, allowing fitting, appraisal and optimization of various data sources, as required in the construction of internally consistent petrological data bases. This approach can also be extended to minerals with λ-transitions and to fluids by considering the Gibbs free energy as a function of pressure P, temperature T and an ordering parameter X_α, so that accurate modelled representation and extrapolation of the thermodynamic properties of large numbers of petrologically significant minerals and coexisting fluids can be attained. The ordering parameter is chosen to denote the equilibrium mole fraction (thermodynamic probability) of ordered clusters (structural units) in a substance when $G(T,P, X_\alpha)$ = min. The procedure is tested on existing experimental data for the system MgO–SiO_2–H_2O. The proposed Gibbs free energy formulation permits thermodynamic properties of minerals, fluids and phase equilibria to be described and extrapolated over a wide range of pressure (0–800 kbar) and temperature (20–3000 K), thus allowing effective use in thermodynamic data bases of petrological interest.

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Introduction

Internally consistent thermodynamic databases (e.g. Karpov et al. 1976; Helgeson et al. 1978; Dorogokupets and Karpov 1984; Berman 1988; Grevel 1995; Holland and Powell 1990, 1998; Chatterjee et al. 1994, 1998; Berman and Aranovich 1996; Gottschalk 1997; Saxena et al. 1993) are widely used for the construction of petrologically relevant phase diagrams, as well as for the modelling of the compositional and physical properties of rocks and minerals at the high pressures and temperatures. In petrological systems, where reactions at depth in the Earth are of foremost interest, pressure, temperature and composition generally are the independent variables of choice, making the Gibbs free energy the most useful stability criterion. In thermodynamic data bases the Gibbs free energy is usually cast in the form

$$G_{P,T} = \Delta H_o - T \cdot S_o + \int_{T_o}^{T} [Cp_{o(T)}]dT$$

$$- T \cdot \int_{T_o}^{T} [Cp_{o(T)}/T]dT + \int_{P_o}^{P} [V_{(P,T)}]dP, \quad (1)$$

where P is pressure, T is temperature, $G_{P,T}$ is the molar Gibbs free energy at given P and T; ΔH_o and S_o are the enthalpy of formation and third-law entropy, respectively, of a substance at standard pressure P_o and temperature T_o; $Cp_{o(T)}$ is the heat capacity as a function of temperature at standard pressure P_o; $V_{(P,T)}$ is the molar volume of a substance as a function of pressure and temperature.

Equation (1) can lead to a direct representation of the Gibbs potential as a function of P and T when $Cp_{o(T)}$ and $V_{(P,T)}$ data are available for integration. Such data are still a major problem, however, and various empirical and semi-empirical power expansion series for $Cp_{o(T)}$ and $V_{(P,T)}$ have been suggested (see, for example, the reviews of Richet et al. 1992 and Saxena et al. 1993) that attempt to systematize the available, usually limited experimental data. Of particular importance is the fact that the form of the fitted polynomial should ideally have a physical significance (e.g. Dubrovinskaya et al. 1997), in order to allow realistic extrapolation beyond the range of the available data base. As discussed in detail by Richet et al. (1992), Saxena et al. (1993) and Dubrovinskaya et al. (1997), this limitation is particularly critical with respect to $Cp_{o(T)}$. While experimental calorimetric measurement leads to isobaric heat capacity $Cp_{o(T)}$, existing models for calculating calorimetric properties of minerals based on lattice dynamics lead instead to the isochoric heat capacity Cv. In addition, the vibration spectra of many of the minerals necessary for a useful petrological data base are still extremely complex and poorly understood. Thus, these models are limited in their effectiveness for providing a physical description of the temperature dependence of Cp_o. All available polynomial fits for $Cp_{o(T)}$ of either experimental data or analogy-based estimates (cf. Richet et al. 1992), although widely used in petrological circles (Berman 1988; Holland and Powell 1990, 1998), are at present entirely empirical.

Theoretical approaches for modelling C_V turn to spectroscopic data and statistical thermodynamics. Molar volume and temperature are taken as independent variables and the Helmholtz free energy $F_{V,T}$ is chosen as the equilibrium potential for minerals (e.g. Kieffer 1985; Polyakov and Kuskov 1994; Dubrovinskaya et al. 1997) and fluids (e.g. Stewart and Jacobson 1989; Saul and Wagner 1989; Hill 1990). Theoretically derived equations for the Helmholtz free energy of solids (e.g. Kieffer 1985; Polyakov and Kuskov 1994; Dubrovinskaya et al. 1997) are primarily based on a statistical mechanical approach employing the canonical partition function in terms of molar volume and temperature that treats minerals as systems of quantum oscillators (e.g. Kubo 1965; Toda et al. 1992; Landau and Lifshitz 1959). Parameterization of these equations is based on either vibration spectra (e.g. Polyakov and Kuskov 1994) or data on isochoric heat capacity and volume (e.g. Dubrovinskaya et al. 1997) at different pressure and temperature. Analytical expressions for any other thermodynamic parameters (e.g. isobaric heat capacity, Gibbs free energy, entropy etc.) can then be derived using standard thermodynamic relations. Thus the Gibbs free energy of a substance at given V and T can be calculated as $G_{V,T} = F_{V,T} - V \cdot \partial F_{V,T}/\partial V$. However, this approach does not lead to a direct formulation of the Gibbs free energy as a function of P and T, as is preferable for a system of petrological interest, nor does it provide a basis for directly fitting experimental $Cp_{o(T)}$ data.

It has recently been shown that an analogous statistical approach (Kut'in and Pyadushkin 1998; Gerya et al. 1998) can be based on a partition function in pressure and temperature (e.g. Kubo 1965; Toda et al. 1992) to obtain expressions for the Gibbs free energy of solids as a function of P and T rather than V and T. Parameterization includes simultaneous regression of $Cp_{o(T)}$ and $V(P,T)$ data, allowing fitting and optimization of various data sources, as required in the construction of an internally consistent petrological data base. This semi-empirical approach can also be extended to minerals with λ-transitions (e.g. Gerya et al. 1998) and to fluids (Gerya and Perchuk 1997), by considering the Gibbs free energy G as a function of pressure, temperature and an ordering parameter, so that accurate modelled representation and extrapolation of the thermodynamic properties of large numbers of petrologically significant minerals and coexisting fluids can be attained. The present paper is intended to summarize this new approach and to test it against well-established data on both the thermodynamic properties of some critical phases of petrological interest and on phase equilibria at high pressures and temperatures.

Summary of the basic method

Derivation of basic equations

For a substance in a crystalline state considered as a system of independent quantum oscillators (e.g. Landau and Lifshitz 1959), the Gibbs free energy can be expressed using the P–T partition function of statistical thermodynamics (Toda et al. 1992). Using a set of approximations for the calculation of the statistical sum over states, the following expression of the molar Gibbs free energy can be obtained (Appendix 1)

$$G_s = H_s - TS_s^o + RT \sum_i^n c_i \ln\{1 - \exp[\Delta H_{si}/RT]\}, \quad (2)$$

where R is the gas constant, H_s and S_s^o are, respectively, molar enthalpy and entropy for a state of zero-point vibrations, n is the number of groups of oscillators considered, c_i is a statistical weight of the i-th group equal to the number of oscillators in the i-th group divided by N_A (Avogadro's number), and ΔH_{si} is the system enthalpy change related to transition between neighbouring energy levels in the i-th group (taken for N_A oscillators). The effects of pressure on H_s and ΔH_{si} are given by

$$H_s = H_s^o + \int_{P_o}^{P} V_s dP, \quad (3)$$

$$\Delta H_{si} = \Delta H_{si}^o + \int_{P_o}^{P} \Delta V_{si} dP, \quad (4)$$

where P_o is standard pressure, H_s^o is molar enthalpy at 0 K and P_o, ΔH_{si}^o is the ΔH_{si} value at P_o, V_s is molar volume at 0 K as a function of pressure, ΔV_{si} is the system volume change due to transition between neighbouring energy levels for the i-th group of oscillators as a function of pressure (taken for N_A oscillators). Theoretical forms of the pressure dependence of V_s and ΔV_{si} are unknown, and thus some well-established semi-empirical functions must be employed. One of the possible choices is the Murnaghan equation, which demonstrates good extrapolation properties in a wide region of pressure at a given temperature (e.g. Zharkov and Kalinin 1971; Saxena et al. 1993):

$$V_s = V_s^o (P_o + \phi)^{1/5}/(P + \phi)^{1/5}, \tag{5}$$

$$\Delta V_{si} = \Delta V_{si}^o (P_o + \phi)^{1/5}/(P + \phi)^{1/5}, \tag{6}$$

where V_s^o is molar volume at 0 K and P_o, ΔV_{si}^o is the ΔV_{si} value at P_o, and ϕ is an empirical parameter approximating the mean effect of attractive interaction between the atoms in the whole pressure range. From Eq (3)–(4), the effect of pressure on H_s and ΔH_{si} is given by

$$H_s = H_s^o + V_s^o \Psi, \tag{7}$$

$$\Delta H_{si} = \Delta H_{si}^o + \Delta V_{si}^o \Psi, \tag{8}$$

where $\Psi = 5/4(P_0 + \phi)^{1/5}[(P + \phi)^{4/5} - (P_0 + \phi)^{4/5}]$.

Standardizing Eq. (2) relative to T_o and P_o with a reduced number of empirical terms ($n \leq 5$, Gerya et al. 1998), and taking into account Eq. (7)–(8), yields

$$G_s = H_{ToPo} - TS_{ToPo} + V_s^o \Psi + \sum_{i=1}^{n \leq 5} c_i[RT\ln(1 - e_i)$$
$$- \Delta H_{si}^o(1 - T/T_o)e_{oi}/(1 - e_{oi}) - RT\ln(1 - e_{oi})], \tag{9}$$

$$S_{ToPo} = -(\partial G_s / \partial T)_{ToPo}$$
$$= S_s^o + \sum_i^n c_i[\Delta H_{si}^o/T_o e_{oi}/(1 - e_{oi}) - R\ln(1 - e_{oi})], \tag{9a}$$

$$H_{ToPo} = H_s^o + \sum_i^n c_i \Delta H_{si}^o e_{oi}/(1 - e_{oi}), \tag{9b}$$

$$e_i = \exp(-\Delta H_{si}/RT) \tag{9c}$$

and

$$e_{oi} = \exp(-\Delta H_{si}^o/RT_o), \tag{9d}$$

where G_{ToPo}, H_{ToPo}, and S_{ToPo} are, respectively, the molar Gibbs free energy, enthalpy and entropy of the substance at standard T_o and P_o. If T_o is taken to be 0 K, the terms in Eq. (9) containing T_o are equal to zero. Equation (9) directly expresses the Gibbs potential of a condensed substance as a function of P and T.

An empirical parameterization of Eq. (9) can now be done using experimental data on isobaric heat capacities and volume measurements. Analytical expressions for Cp and V can be obtained from Eq. (9) as follows

$$C_p = -T(\partial^2 G_s/\partial T^2) = \sum_{i=1}^{n \leq 5} c_i \Delta H_{si}^2/RT^2[e_i/(1 - e_i)^2], \tag{10}$$

$$V = \partial G_s/\partial P = [\sum_{i=1}^{n \leq 5} c_i \Delta V_{si}^o e_i/(1 - e_i)$$
$$+ V_s^o](P_o + \phi)^{1/5}/(P + \phi)^{1/5}. \tag{11}$$

Calculated examples

As an example of the applicability of Eqs. (9)–(11) for the description of the thermodynamic properties of crystalline substances, data for periclase, brucite, coesite and stishovite (Table 1) are considered. With $n = 3$, $S_s^o = 0$ (according to Nernst's law), $P_o = 1$ bar and $T_o = 298.15$ K, an equation of molar Gibbs free energy for these minerals takes the form (Gerya et al. 1998):

$$G_s = H_{298,1} + V_s^o \Psi + \sum_{i=1}^{3} c_i[RT\ln(1 - e_i)$$
$$- \Delta H_{si}^o e_{oi}/(1 - e_{oi})], \tag{12}$$

where $e_i = \exp[-(\Delta H_{si}^o + \Delta V_{si}^o \Psi)RT]$, $e_{oi} = \exp(-\Delta H_{si}^o/R298.15)$, $\Psi = 5/4(P_o + \phi)^{1/5}[(P + \phi)^{4/5} - (1 + \phi)^{4/5}]$. Entropy S_{ToPo} is absent from Eq. (12) since $S_s^o = 0$ and all other terms in Eq. (9a) are cancelled by corresponding terms in Eq. (9). Third-law entropy can be calculated according to Eq. (9a) assuming that low-temperature heat capacity (20–298 K) is accurately represented by Eq. (10).

The results for the parameters of Eq. (12) are listed in Table 2. The derivation of these internally consistent thermodynamic data was performed by a non-linear least-squares method. Processing of the experimental data was done in cyclic fashion with quality control of the refined parameters. The measured parameters are reproducible within experimental error. To illustrate this, the calculated results for isobaric heat capacity and volume are plotted against the original experimental data in Figs. 1–4. It is seen that by comparison to the power expansion formulations used in petrological data bases (e.g. Berman 1988; Holland and Powell 1998), Eq. (12) allows a better fit of isobaric heat capacities and volumes over a very wide region of pressure (0–800 kbar) and temperature (20–3000 K). Equation (2) requires that c_i in Eq. (12) should sum to $3v$, where v is the number of atoms in the formula unit. This is fulfilled for coesite and stishovite (the sum is 9), but not quite for brucite (the sum is 14.6 instead of 15) and periclase (the sum is 6.6 instead of 6). These discrepancies are due to the relatively low value of n (= 3) chosen in Eq. (12), which may not be sufficient to

Table 1 Source of experimental data used in this study

Starting data	References
Isobaric heat capacity of quartz	Gurevitch and Khlyustov (1979); Watanabe (1982); Hemingway (1987); Grønvold et al. (1989); Hemingway et al. (1991); Akaogi et al. (1995)
Molar volume of quartz	Jay (1933); Ackermann and Sorell (1974); Danielsson et al. (1976); Lager et al. (1982); Olinger and Halleck (1976); Jorgensen (1978); d'Amour et al. (1979); Levien et al. (1980); Hazen et al. (1989); Kihara (1990); Vaidya et al. (1973); Glinnemann et al. (1992)
Adiabatic modulus of quartz, $(\partial T/\partial P)_S$	Boehler et al. (1979); Boehler (1982)
Relative molar enthalpy of quartz	Richet et al. (1982)
Isobaric heat capacity of coesite	Holm et al. (1967); Akaogi et al. (1995)
Molar volume of coesite	Bassett and Barnett (1970); Levien and Prewitt (1981) Galkin et al. (1987); Smyth et al. (1987)
Relative molar enthalpy of coesite	Holm et al. (1967); Akaogi and Navrotsky 1984; Akaogi et al. (1995)
Isobaric heat capacity of stishovite	Holm et al. (1967); Akaogi et al. (1995)
Molar volume of stishovite	Bassett and Barnett (1970); Liu et al. (1974); Olinger (1976); Sato (1977); Endo et al. (1986); Doroshev et al. (1987); Tsuchida and Yagi (1989); Ross et al. (1990) Suito et al. (1996)
Enthalpy of phase transition quartz-coesite	Holm et al. (1967); Akaogi and Navrotsky (1984); Kuskov et al. (1991); Akaogi et al. (1995)
Phase transition α-quartz - β-quartz	Gibson (1928); Yoder (1950); Cohen and Klement (1967); Koster van Groos and Ten Heege (1973); Mirwald and Massone (1980b); Shen et al. (1993)
Phase transition quartz—coesite	Boyd and England (1960); Kitahara and Kennedy (1964); Mirwald and Massone (1980a,b); Akella (1979); Bohlen and Boettcher (1982); Ishbulatov and Kosyakov (1990); Bose and Ganguly (1995)
Phase transition coesite–stishovite	Akimoto and Syono (1969); Yagi and Akimoto (1976); Suito (1977); Zhang et al. (1993), (1996); Serghiou et al. (1995)
Water: tabulated data on molar Gibbs free energy, molar entropy and molar volume of water at $T = 0$–1000 °C and $P = 1$–10 000 bar; tabulated P–V–T data on liquid-gas transition	Saul and Wagner (1989)
Isobaric heat capacity of periclase	Giauque and Archibald (1937); Barron et al. (1959); Glushko et al. (1979); Krupka et al. (1979); Watanabe (1982)
Molar volume of periclase	Reeber et al. (1995); Fiquet et al. (1999); Fei (1999) Dewaele et al., (2000); Zhang (2000)
Adiabatic modulus of periclase $(\partial T/\partial P)_S$	Boehler (1982)
Relative molar enthalpy of periclase	Richet and Fiquet (1991)
Isobaric heat capacity of brucite	Giauque and Archibald (1937); Glushko et al. (1979)
Molar volume of brucite	Chakoumakos et al. (1997); Catti et al. (1995); Parise et al. (1994); Fei and Mao (1993); Nagai et al. (2000); Xia et al. (1998)
Phase transition brucite = periclase + water	Franz (1982); Schramke et al. (1982); Johnson and Walker (1993); Aranovich and Newton (1996)

reflect the actual number of different groups of oscillators.

Modification to include minerals with λ-transitions

Derivation of basic equations

Some petrologically important phases such as quartz demonstrate specific changes in thermodynamic properties that are related to a λ-transition not accounted for in Eq. (9). Most approaches attempt to describe this effect in terms of the formalism of Landau theory (e.g. Carpenter et al. 1998; Dove 1997; Holland and Powell 1998). Landau theory (e.g. Landau and Lifshitz 1959) suggests that the Gibbs potential of a crystalline phase in the region of the λ-transition can be considered as a function of P, T and an order parameter η. The equilibrium order parameter corresponds to a minimum of the Gibbs free energy $G(T,P,\eta) = \min$. This general

formalism is consistent with thermodynamic concepts of homogeneous equilibria in crystals (Thompson 1969) widely developed for phases of petrological interest (e.g. Holland and Powell 1996). A similar approach has recently been applied to the λ-transition in quartz (Gerya et al. 1998).

A thermodynamic process related to a λ-transition in a one-component mineral can be viewed as an internal ordering reaction (transition)

$$a\mathrm{A} = \alpha, \tag{13}$$

where A is a disordered cluster (structural unit), $\alpha = \mathrm{A}_a$ is an ordered cluster (structural unit), a is the stoichiometric coefficient. The thermodynamic equilibrium for Reaction (transition) 13 is given by

$$\Delta G_{\mathrm{ord}} = \mathrm{R}T\ln(K_{\mathrm{ord}}) + \Delta G_{\mathrm{ord}}^{\mathrm{o}} + \Delta G_{\mathrm{ord}}^{\mathrm{e}} = 0, \tag{14}$$

where $K_{\mathrm{ord}} = X_\alpha/(X_\mathrm{A}^a)$ and $X_\mathrm{A} + X_\alpha = 1$. X_A and X_α are the mole fractions (thermodynamic probabilities) of the disordered and ordered clusters (structural units),

Table 2 Calculated parameters of Eqs. (12), (20) and (30) for the molar Gibbs free energy of minerals and water

Parameter	Coesite	Stishovite	Brucite	Periclase	Quartz	Water
$H_{298,1}$, J	−907051.35	−870123.92	−925267.08	−601500.00[a]	−910712.59[a]	−286831.56[a]
$S_{298,1}$, J K^{-1}	–	–	–	–	–	65.188
V_s^o, J bar^{-1}	2.05333	1.40010	2.43162	1.12228	2.25888	1.71382
ϕ, bar	217664	612340	98040	301795	71662	6209
c_1	1.44913	0.28816	1.87663	1.96612	1.42569	7.23576
c_2	3.71385	2.73177	8.55012	4.12756	3.50283	0.31482
c_3	3.83702	5.98007	4.16639	0.53690	4.07148	–
ΔH_{s1}^o, J	1435.64	1179.01	1637.57	2966.88	1278.08	4586.46
ΔH_{s2}^o, J	4099.77	3845.99	4403.89	5621.69	3911.05	–
ΔH_{s3}^o, J	10479.16	8042.74	11614.44	27787.19	10469.21	–
ΔV_{s1}^o, J bar^{-1}	0.00158600	0.00233400	0.00541752	0.00352971	0.00312581	0.04310884
ΔV_{s2}^o, J bar^{-1}	$=\Delta V_{s1}^o$	$=\Delta V_{s1}^o$	$=\Delta V_{s1}^o$	$=\Delta V_{s1}^o$	$=\Delta V_{s1}^o$	–
ΔV_{s3}^o, J bar^{-1}	$=\Delta V_{s1}^o$	$=\Delta V_{s1}^o$	0.07026587	0.19849568	$=\Delta V_{s1}^o$	–
ΔH^o_{ord}, J	–	–	–	–	−2636.90	−44838.80
ΔS^o_{ord}, J K^{-1}	–	–	–	–	–	−122.397
ΔCp^o_{ord}, J K^{-1}	–	–	–	–	–	21.486
ΔV^o_{ord}, J bar^{-1}	–	–	–	–	−0.127829	–
W^H_1, J^{-1}	–	–	–	–	14255.08	−28793.19
W^S_1, J K^{-1}	–	–	–	–	–	−11.704
W^{Cp}_1, J K^{-1}	–	–	–	–	–	5.086
W^V_1, J bar^{-1}	–	–	–	–	0.633504	–
$\Delta H_{s\lambda}^o$, J	–	–	–	–	12947.71	–
$\Delta V_{s\lambda}^o$, J bar^{-1}	–	–	–	–	0.242077	–

[a] The $H_{298,1}$ value has been adjusted to obtain the enthalpies of formation at 298.15 K and 1 bar, as recommended by CODATA (1978)

respectively. ΔG^o_{ord} and ΔG^e_{ord} are changes of the standard and excess Gibbs free energy, respectively, due to Reaction (13). According to our formalism, ordered/disordered clusters need not always be static (long-lived) structural features, but may reflect dynamic (short-lived) variations due to the thermal vibration of atoms (e.g. Kihara 1990). This does not preclude a uniform thermodynamic treatment, but instead changes the interpretation of the ordering parameter X_α. For static features this parameter represents the mole fraction of ordered clusters, while for dynamic variations it stands for the thermodynamic probability of finding the given structural units in the ordered state. The additional molar Gibbs free energy relative to the ordered state ($X_\alpha = 1$) is defined as (Gerya et al. 1998):

$$G_\alpha = \{RT[(1-X_\alpha)\ln(1-X_\alpha) + X_\alpha \ln(X_\alpha)] - \Delta G^o_{ord}(1-X_\alpha)/a + \Delta G^e_{ord}\}/[1 + X_\alpha(a-1)], \tag{15}$$

where $\Delta G^o_{ord} = \Delta H^o_{ord} + \Delta V^o_{ord}\Psi$, $G^e_{ord} = W^G(1-X_\alpha)$ (X_α), $W^G = W^H + W^V\Psi$.

G^e_{ord} is the integral excess Gibbs free energy of mixing of ordered and disordered clusters expressed using the Margules formalism (e.g. Thompson 1969), with the expressions for ΔG^o_{ord} and W^G formulated by analogy to Eq. (7).

If the λ-transition leads to significant changes in the thermal vibrations of atoms, this must be taken into account in the vibrational part of the Gibbs potential. The corresponding formulation derived from the P–T partition function by analogy to Eq. (9) takes the form (see Appendix 2)

$$G_s = H_{ToPo} - TS_{ToPo} + V_s^o$$
$$+ \sum_{i=1}^{n\leq 5} c_i\{RT\ln\{(1-e_{\alpha i})(1-e_{\beta i})/[(1-e_{\beta i}) + e_{\lambda i}(e_{\beta i} - e_{\alpha i})]\} - \Delta H_{si\alpha}^o(1-T/T_o)e_{o\alpha i}/(1-e_{o\alpha i})$$
$$- RT\ln(1-e_{o\alpha i})\}, \tag{16}$$

where $S_{ToPo} = -(\partial G_s/\partial T)_{ToPo}$

$$= S_s^o + \sum_i^n c_i[\Delta H_{si}^o/T_o\, e_{o\alpha i}/(1-e_{o\alpha i}) - R\ln(1-e_{o\alpha i})],$$

$$H_{ToPo} = H_s^o + \sum_i^n c_i\Delta H_{si}^o e_{o\alpha i}/(1-e_{o\alpha i}),$$

$$e_{\alpha i} = \exp(-\Delta H_{si\alpha}/RT), \quad e_{\beta i} = \exp(-\Delta H_{si\beta}/RT),$$

$$e_{\lambda i} = \exp(-\Delta H_{si\lambda}/RT), \quad e_{o\alpha i} = \exp(-\Delta H_{si\alpha}^o/RT_o),$$

$$\Delta H_{si\alpha} = \Delta H_{si\alpha}^o + \Delta V_{si\alpha}^o\Psi, \quad \Delta H_{si\beta} = \Delta H_{si\beta}^o + \Delta V_{si\beta}^o\Psi,$$

and $$\Delta H_{si\lambda} = \sum_{k=0}^2 (\Delta H_{si\lambda k}^o + \Delta V_{si\lambda k}^o\Psi)\,(X_\alpha)^k.$$

$\Delta H_{si\alpha}$ and $\Delta H_{si\beta}$ are values of ΔH_{si} for ordered and disordered substances, respectively; $\Delta H_{si\lambda}$ is the apparent enthalpy parameter dependent on X_α and related to the order–disorder transition for the i-th group of oscillators.

Under isothermal-isobaric conditions, an equilibrium in a non-reacting phase is given by

Fig. 1a–c Comparison of
calculated isobaric heat
capacity (**a**) and molar
volume (**b,c**) of coesite with
measured data
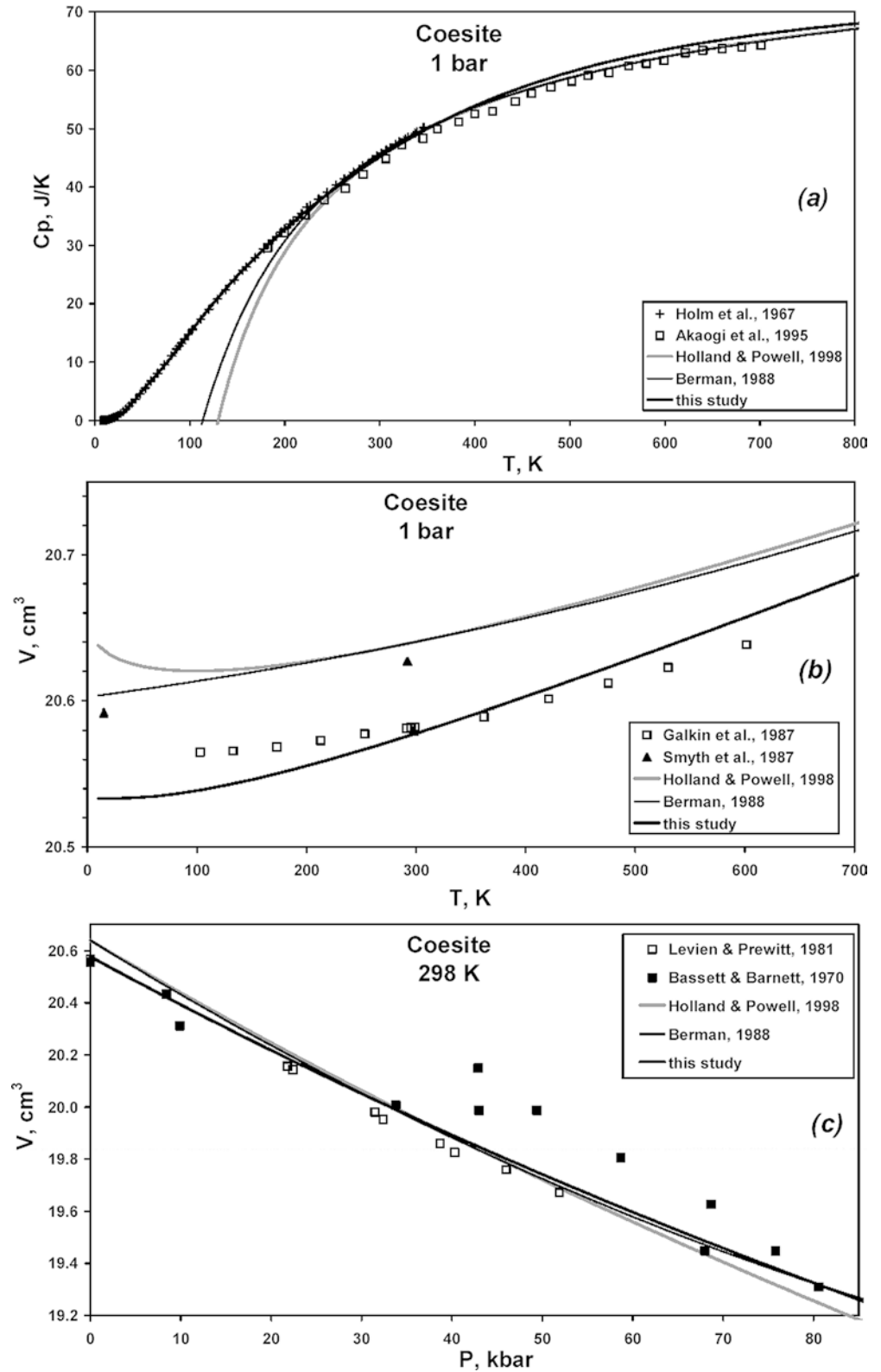
$$G_{s+\alpha} = G_s + c_\alpha G_\alpha = \min, \qquad (17)$$

$$\partial G_{s+\alpha}/\partial X_\alpha = 0, \qquad (18)$$

where $G_{s+\alpha}$ is the molar Gibbs free energy of a substance with a λ-transition, G_s is given either by Eq. (7)

when changes in thermal vibrations are insignificant, or by Eq. (16), when these changes must be taken into account, and c_α is the number of degrees of freedom corresponding to the ordering Reaction (13). X_α can be considered to be equivalent to the ordering parameter η

Fig. 2a–c Comparison of calculated isobaric heat capacity (**a**) and molar volume (**b,c**) of stishovite with measured data
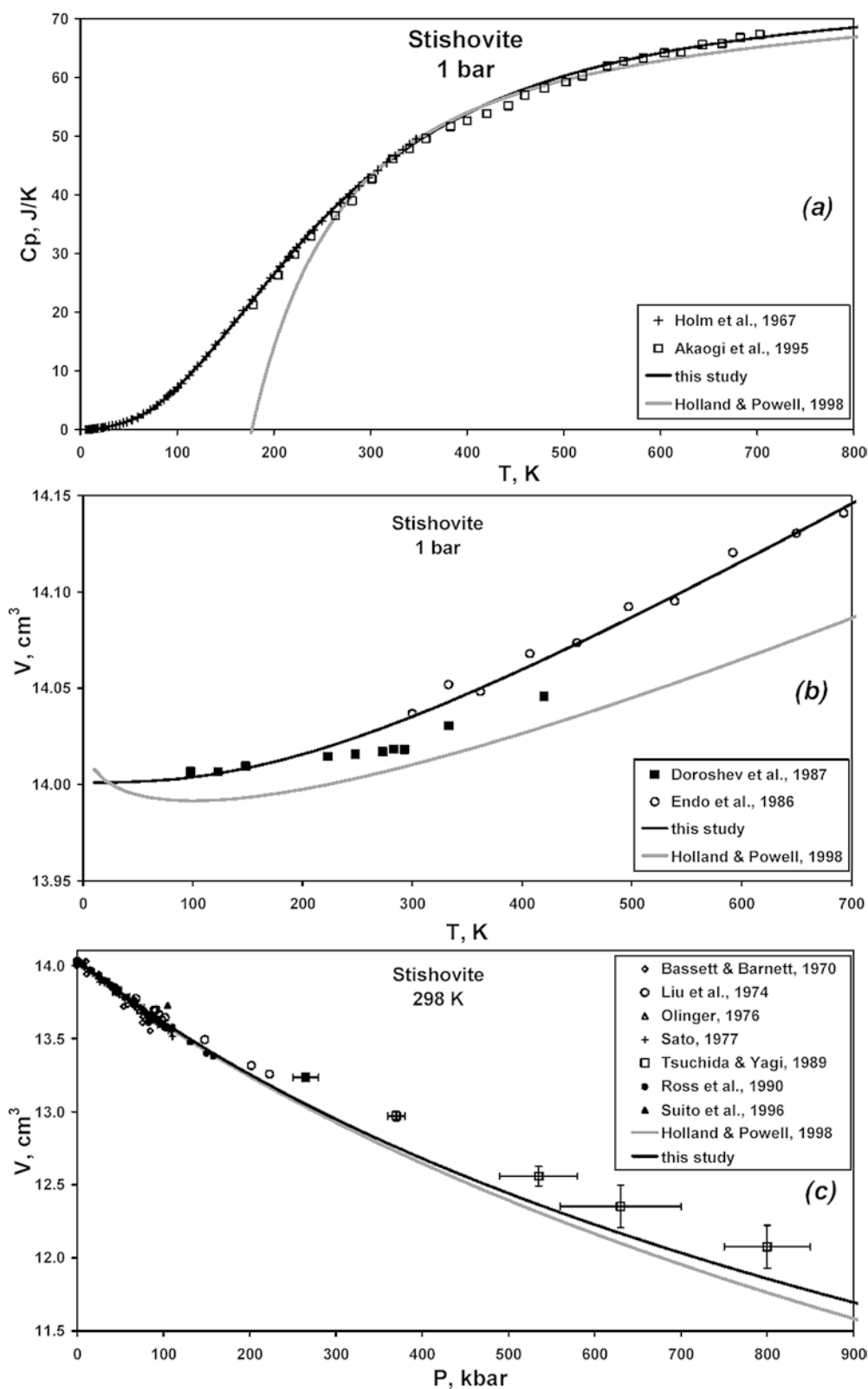
above, which tends to a maximum ($X_\alpha^{max} \leq 1$) in the ordered phase with decreasing temperature, while, with increasing temperature, it tends to a minimum ($X_\alpha^{min} \geq 0$) in the disordered phase.

Application to quartz

As an example of the applicability of Eqs. (13)–(18), to the description of the thermodynamic properties of

Fig. 3a–c Comparison of calculated isobaric heat capacity (**a**) and molar volume (**b,c**) of periclase with measured data
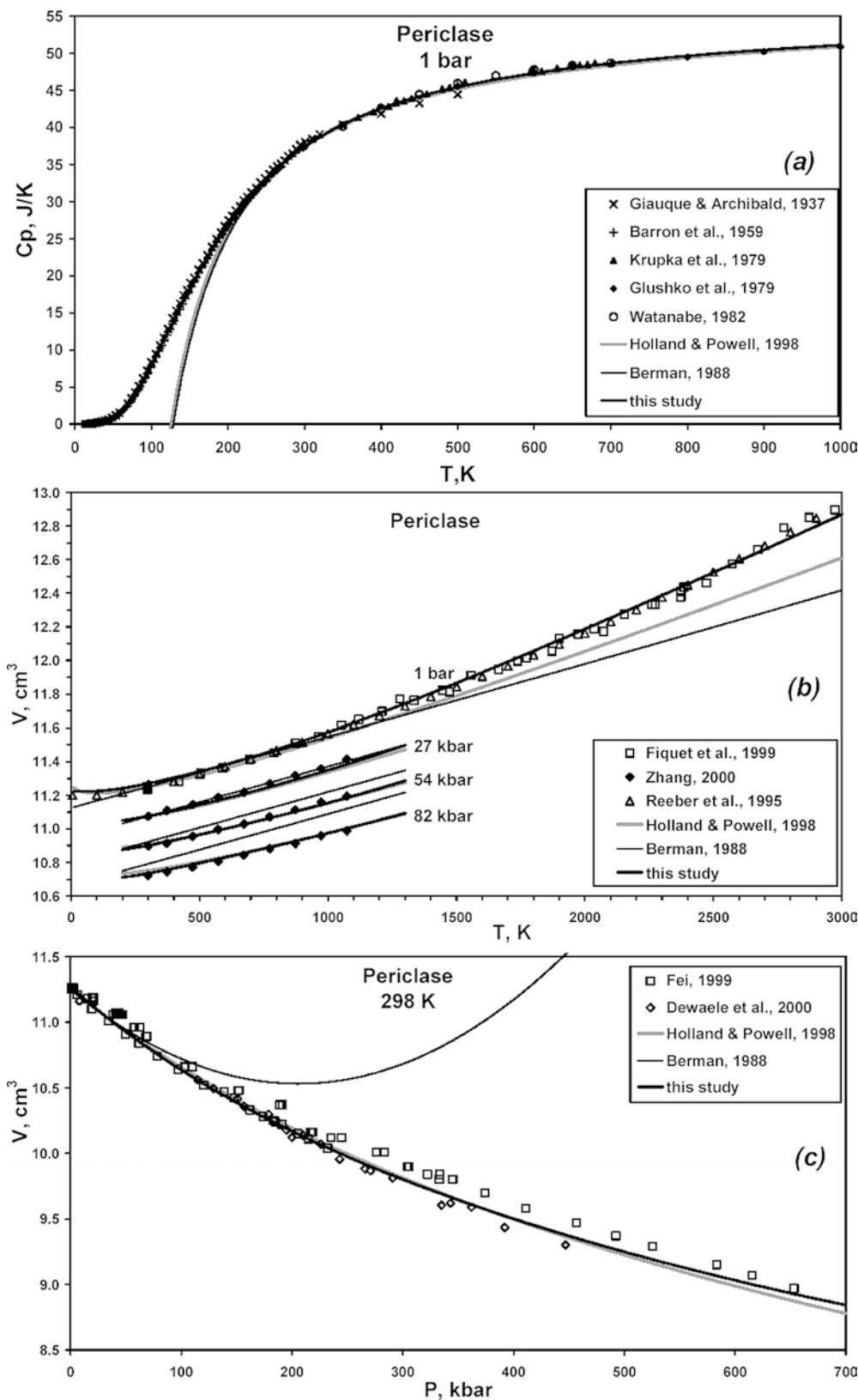
minerals with a λ-transition, the results of their parameterization can be considered for quartz. Ordering–disordering phenomena in quartz are well studied over a wide range of *P–T* conditions and manifest themselves in anomalous behaviour of heat capacity and thermal expansion, thus providing tight

Fig. 4a–c Comparison of calculated isobaric heat capacity (**a**) and molar volume (**b,c**) of brucite with measured data
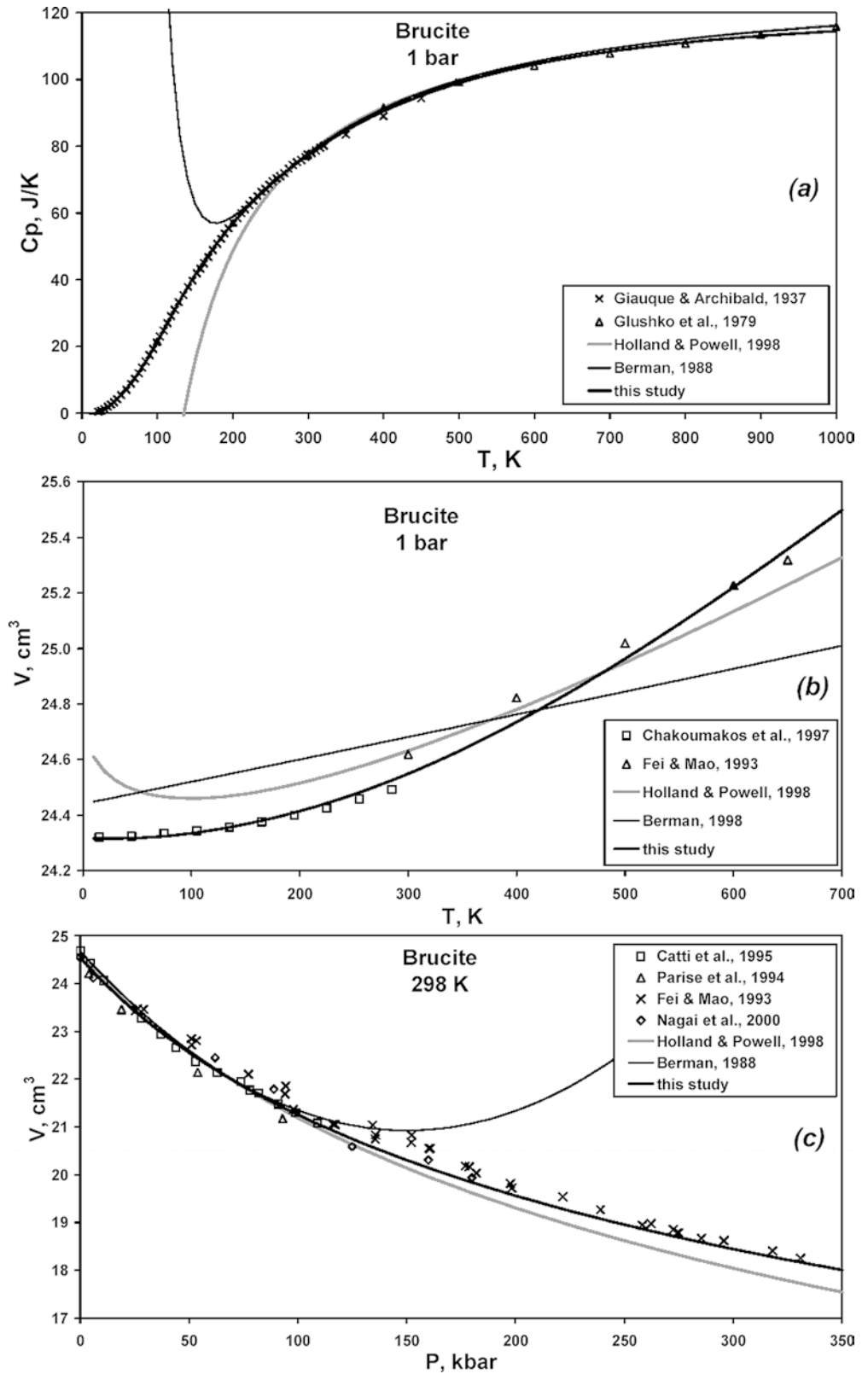
constraints on the proposed model (e.g. Dorogokupets 1995). The data for quartz were treated using Eqs. (15)–(18), with ordering represented by the following homogeneous ordering reaction

$$3SiO_2(Qtz_\beta) = Si_3O_6(Qtz_\alpha), \qquad (19)$$
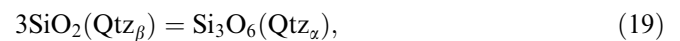
where Qtz_β and Qtz_α are, respectively, disordered and ordered quartz clusters (e.g. Castex and Madon 1995;

Spearing et al. 1992). Using $c_\alpha = 1$ in Eq. (17) and $n = 3$, $V_{si\alpha}{}^o = V_{si}{}^o$, $V_{si\beta}{}^o = 0$, $S_s{}^o = 0$ (according to Nernst's law), $P_o = 1$ bar and $T_o = 298.15$ K in Eq. (16), the Gibbs free energy equation for quartz takes the following semi-empirical form (Gerya et al. 1998)

$$G_{s+\alpha} = H_{298,1} + V_s{}^o \Psi$$

$$+ \sum_{i=1}^{3} c_i \{ RT \ln\{(1 - e_{\alpha i})(1 - e_{\beta i})/[(1 - e_{\beta i})$$
$$+ e_\lambda(e_{\beta i} - e_{\alpha i})]\} - \Delta H_{si}{}^o e_{oi}/(1 - e_{oi})\}$$
$$+ \{ RT[X_\alpha \ln(X_\alpha) + (1 - X_\alpha)\ln(1 - X_\alpha)]$$
$$- (\Delta H^o_{ord} + \Delta V^o_{ord}\Psi)(1 - X_\alpha)/3$$
$$+ (W_1^H + W_1^V \Psi)(1 - X_\alpha)X_\alpha\}/(1 + 2X_\alpha), \quad (20)$$

where $e_{\alpha i} = \exp[-(\Delta H_{si}{}^o + \Delta V_s{}^o \Psi)/RT]$, $e_{\beta i} = \exp(-\Delta H_{si}{}^o/RT)$, $e_{oi} = \exp(-\Delta H_{si}{}^o/R298.15)$, $e_\lambda = \exp[-(\Delta H_{s\lambda}{}^o X_\alpha{}^2 + \Delta V_{s\lambda}{}^o \Psi)/RT]$, $\Psi = 5/4(P_o + \phi)^{1/5}[(P + \phi)^{4/5} - (1 + \phi)^{4/5}]$. X_α is the mole fraction of ordered Si_3O_6 clusters. The empirical parameters obtained for Eq. 20 are presented in Table 2.

Equation (20) allows an accurate description of both experimental heat capacity and volume of α- and β-quartz over a wide region of P and T that includes the λ-transition (Fig. 5). By comparison with the formulations of Berman (1988), Dorogokupets (1995) and Holland and Powell (1998), Eq. 20 demonstrates a superior fit of the available experimental data (Fig. 5).

Gibbs potential of fluids

Derivation of basic equations

Fundamental, precise descriptions of the thermodynamic properties of fluid over a wide P–T interval, including the two-phase region, are traditionally based on the Helmholtz potential and related $P = f(V,T)$ equations of state (e.g. Stewart and Jacobson 1989; Saul and Wagner 1989; Hill 1990). However, it was recently shown (Gerya and Perchuk 1997) that a similar description can be based on the Gibbs potential. The phenomenological approach suggested by Gerya and Perchuk (1997) uses the concept of an internal reaction of association of molecules to form dynamic (short-lived) clusters in fluids. Such an approach is well developed theoretically for describing the hydrogen bonding in supercritical fluids (e.g. Luck 1980; Gupta et al. 1992) and its potential applicability to any fluid has been demonstrated (Barelko et al. 1994; Gerya and Perchuk 1997).

According to Barelko et al. (1994), the dynamic process of association of molecules in any supercritical fluid can be considered as a chain clusterization reaction

$$A_1 + A_n = A_{n+1}, \quad (21)$$

where A_1 stands for a monomer, and A_n and A_{n+1} denote clusters of dimensions n and $n+1$. The thermodynamic equilibrium of Reaction (21) is given by

$$\Delta G_{cls} = RT \ln[K_{cls(n)}] + \Delta G^o_{cls(n)} + \Delta G^e_{cls(n)} = 0, \quad (22)$$

where $K_{cls(n)} = X_{n+1}/(X_1 X_n)$ and $\sum_{n=1}^{\infty} X_n = 1$; X_1, X_n, and X_{n+1} are the mole fractions (thermodynamic probabilities) of clusters of dimension 1 (i.e. monomers), n and $n + 1$, respectively; $\Delta G^o_{cls(n)}$ and $\Delta G^e_{cls(n)}$ are changes of the standard and excess Gibbs free energy, respectively, due to Reaction (21). The additional molar Gibbs free energy relative to the associated ($X_1 = 0$, $X_\infty = 1$) state is given by

$$G_\alpha = \sum_{n=1}^{\infty} X_n[RT \ln(X_n) + n(G^o_1 + G^e_1)$$
$$+ \sum_{m=1}^{n-1}(\Delta G^o_{cls(m)} + \Delta G^e_{cls(m)})]/\sum_{n=1}^{\infty} nX_n - [G^o_1$$
$$+ \sum_{m=1}^{\infty-1} \Delta G^o_{cls(m)}/\infty], \quad (23)$$

where G^o_1 and G^e_1 are standard and excess Gibbs free energy of monomers, respectively. When the equilibrium constant of Reaction (22) is assumed to be independent of n, summation in Eq. (23), using Eq. (22), yields

$$G_\alpha = \{ RT[(1 - X_1)\ln(1 - X_1) + X_1 \ln(X_1)]$$
$$- \Delta G^o_{cls}X_1 + G^e\}, \quad (24)$$

where ΔG^o_{cls} is the change of standard Gibbs free energy in Reaction (21) (independent of n), G^e is the excess molar energy of mixing, related to the presence of different clusters in the fluid. A similar equation was obtained by Gerya and Perchuk (1997) by treating the dynamic association process as a simple, short-term "ordering" transition

$$Gas = Liq, \quad (25)$$

where Gas stands for a molecule in the "gas-like" (free, "disordered") mode, and Liq denotes a molecule in the "liquid-like" (associated, "ordered") mode. According to Reaction (25) the additional molar Gibbs free energy relative to the associated ($X_{Gas} = 0$, $X_{Liq} = 1$) state is given by

$$G_\alpha = RT[X_{Liq} \ln(X_{Liq}) + X_{Gas}\ln(X_{Gas})] - \Delta G^o_{ord}X_{Gas} + G^e, \quad (26)$$

where ΔG^o_{ord} is a change of standard Gibbs free energy in "ordering" Reaction (25). Thus, from the viewpoint of thermodynamics, both considerations are equivalent and yield similar results.

A semi-empirical formulation of the last two terms in Eq. (26) yields (see Appendix 3)

$$G_\alpha = RT[X_{Liq} \ln(X_{Liq}) + (1 - X_{Liq})\ln(1 - X_{Liq})]$$
$$+ (1 - X_{Liq})RT \ln[(P + \phi X_{Liq}{}^2)/P_o]$$
$$- (1 - X_{Liq})\{\Delta H^o_{ord} - T\Delta S^o_{ord}$$
$$+ \Delta C^o_{P\ ord}[T - T_o - T \ln(T/T_o)]\}$$
$$+ \{W_1^H - TW_1^s + W_1^{Cp}[T$$
$$- T_o - T \ln(T/T_o)]\}X_{Liq}(1 - X_{Liq}), \quad (27)$$

Fig. 5a–c Comparison of calculated isobaric heat capacity (**a**) and molar volume (**b,c**) of quartz with measured data
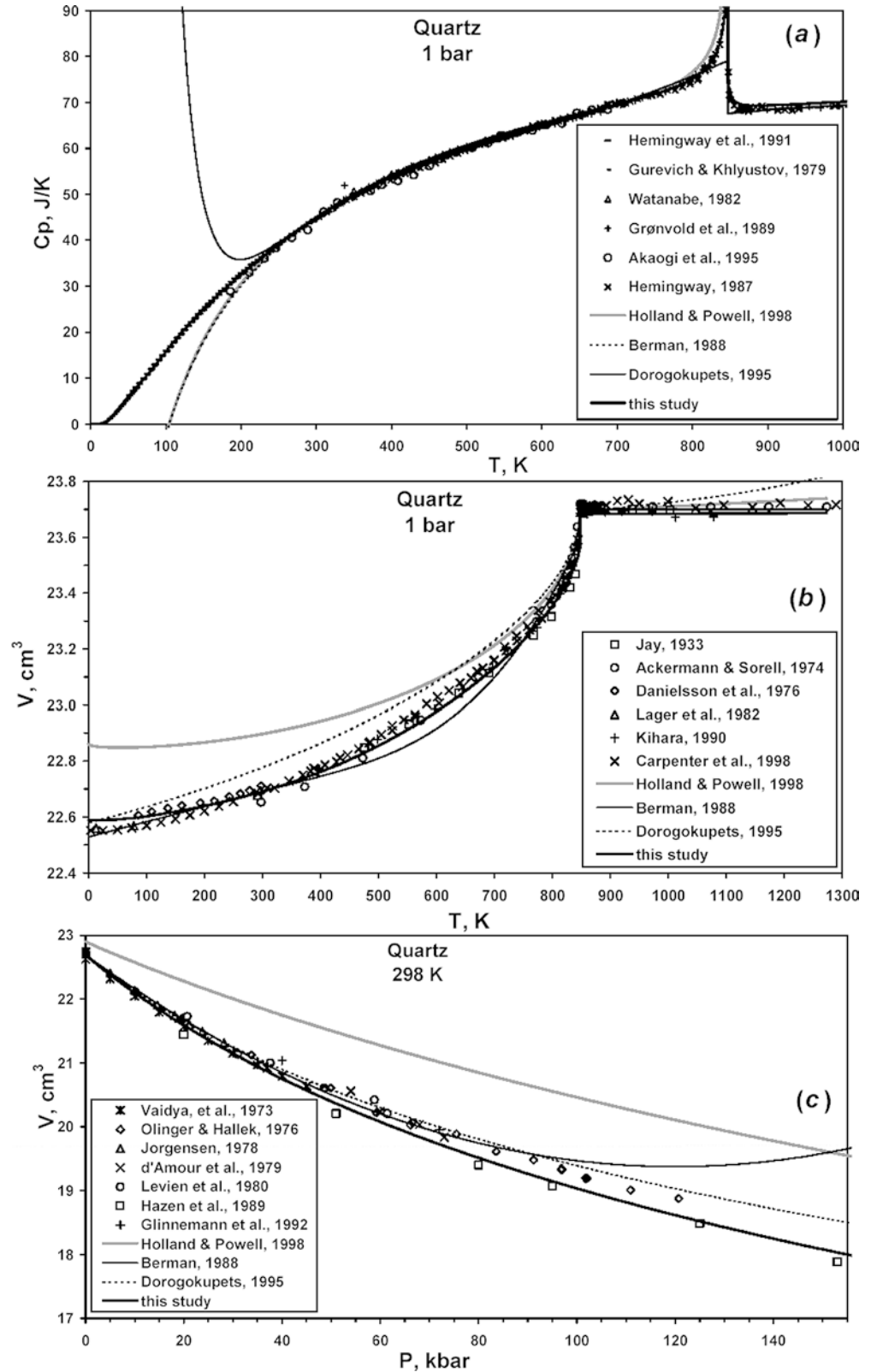
where ΔH^o_{ord}, ΔS^o_{ord}, $\Delta C_{P}{}^o{}_{ord}$ are standard enthalpy, entropy and heat capacity effects of Reaction (25), W^H_1, W^S_1, W^{Cp}_1 are enthalpy, entropy and heat capacity Margules parameters.

By analogy with minerals, a standard Gibbs free energy, G_s, of fluid in fully associated "liquid-like" state ($X_{Gas} = 0$, $X_{Liq} = 1$), considered as a system of quantum oscillators, can be approached by Eq. (9). Under

Fig. 6a–c Comparison of calculated volume (**a**), entropy (**b**) and Gibbs energy (**c**) of water with tabulated data (Saul and Wagner 1989)
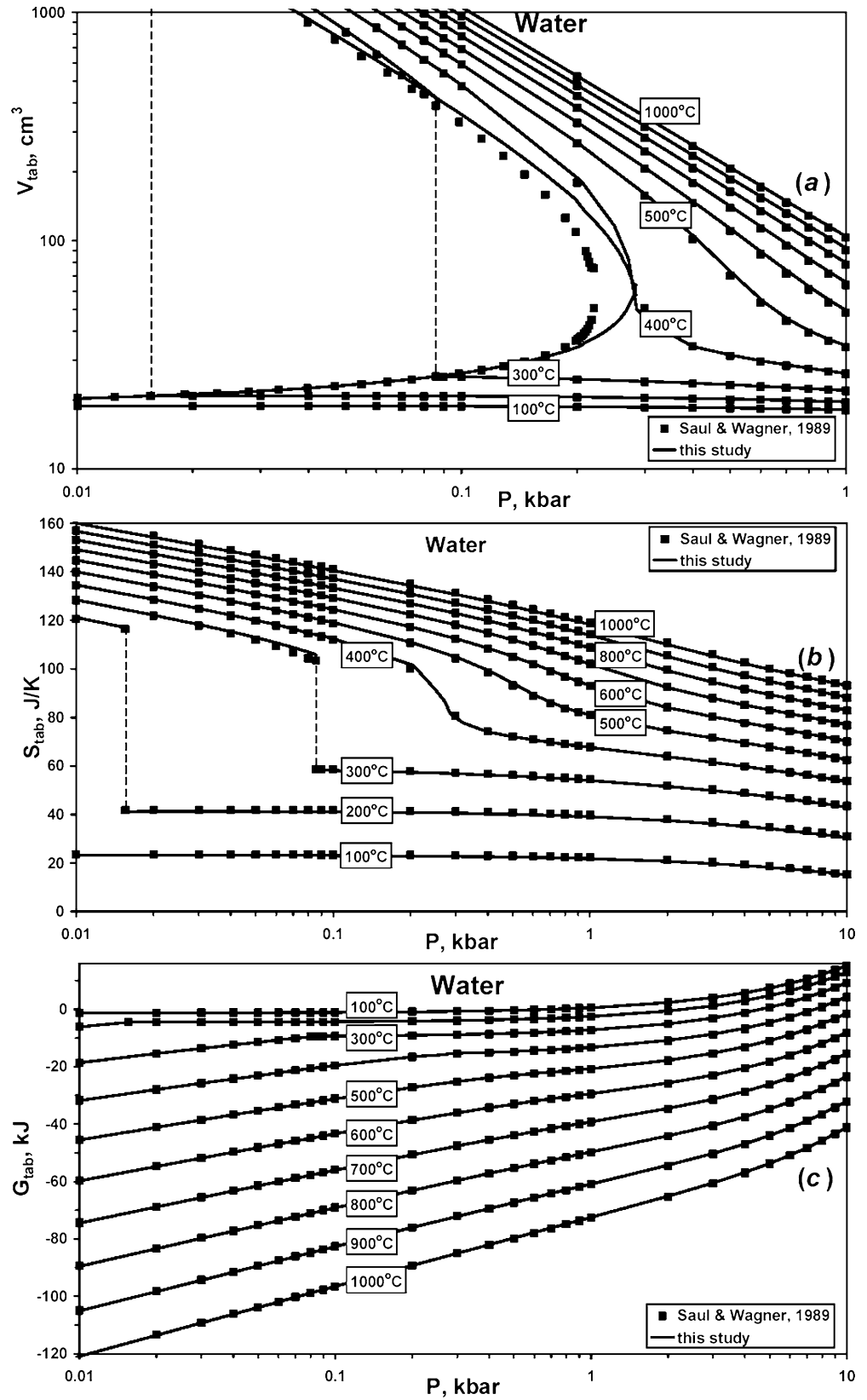
isothermal-isobaric conditions, equilibrium in a one-phase fluid is given by

$$G_{s+\alpha} = G_s + G_\alpha = \text{min} \qquad (28)$$

$$\partial G_\alpha / \partial X_{Liq} = 0. \qquad (29)$$

where $G_{s+\alpha}$ is the molar Gibbs free energy of a fluid, and G_s is given by Eq. 9.
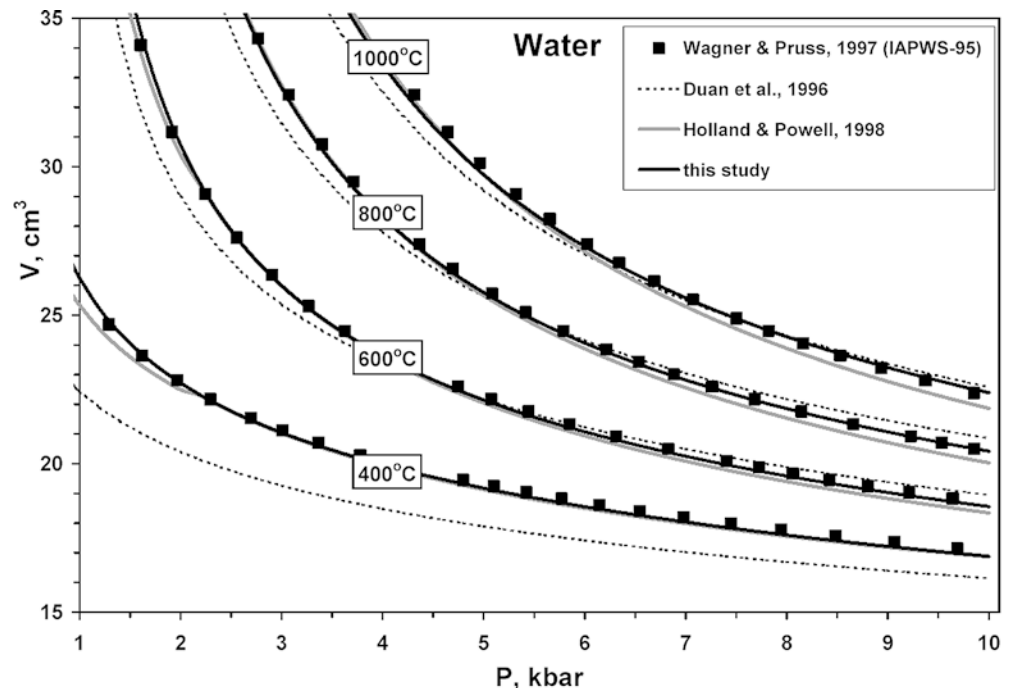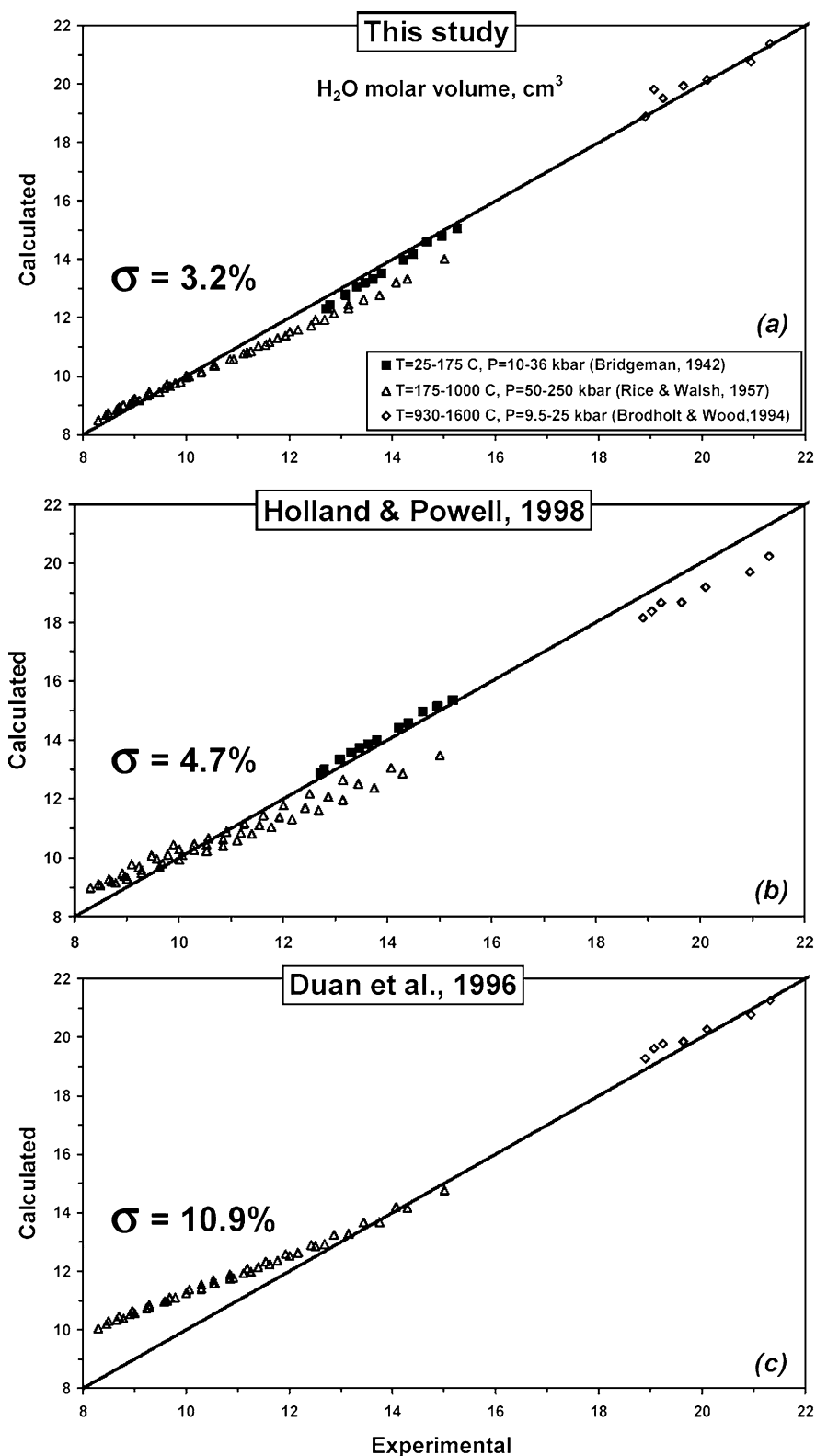
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Fig. 8a–c Comparison of the extrapolated molar volumes of water with results of the independent volumetric (Bridgeman 1942; Brodholt and Wood 1994) and shock-wave (Rice and Walsh 1957) experiments. Different diagrams show the volumes calculated using Eq. (30) (**a**), and PVT formulations suggested by Holland and Powell (1998) (**b**) and Duan et al. (1996) (**c**)

Gibbs free energy described here over a wide range of pressures and temperatures. The extrapolation properties of the above equations can be simultaneously tested for both minerals and the coexisting aqueous fluid. All calculations are inherently based on internally consistent data on the basis of non-linear least-squares analysis.

We considered several experimentally studied equilibria involving aqueous fluid, quartz, coesite, stishovite, periclase, and brucite. Figure 9 show the results

Fig. 9a, b Comparison of phase boundaries calculated for quartz (**a**) and water (**b**) with experimental data
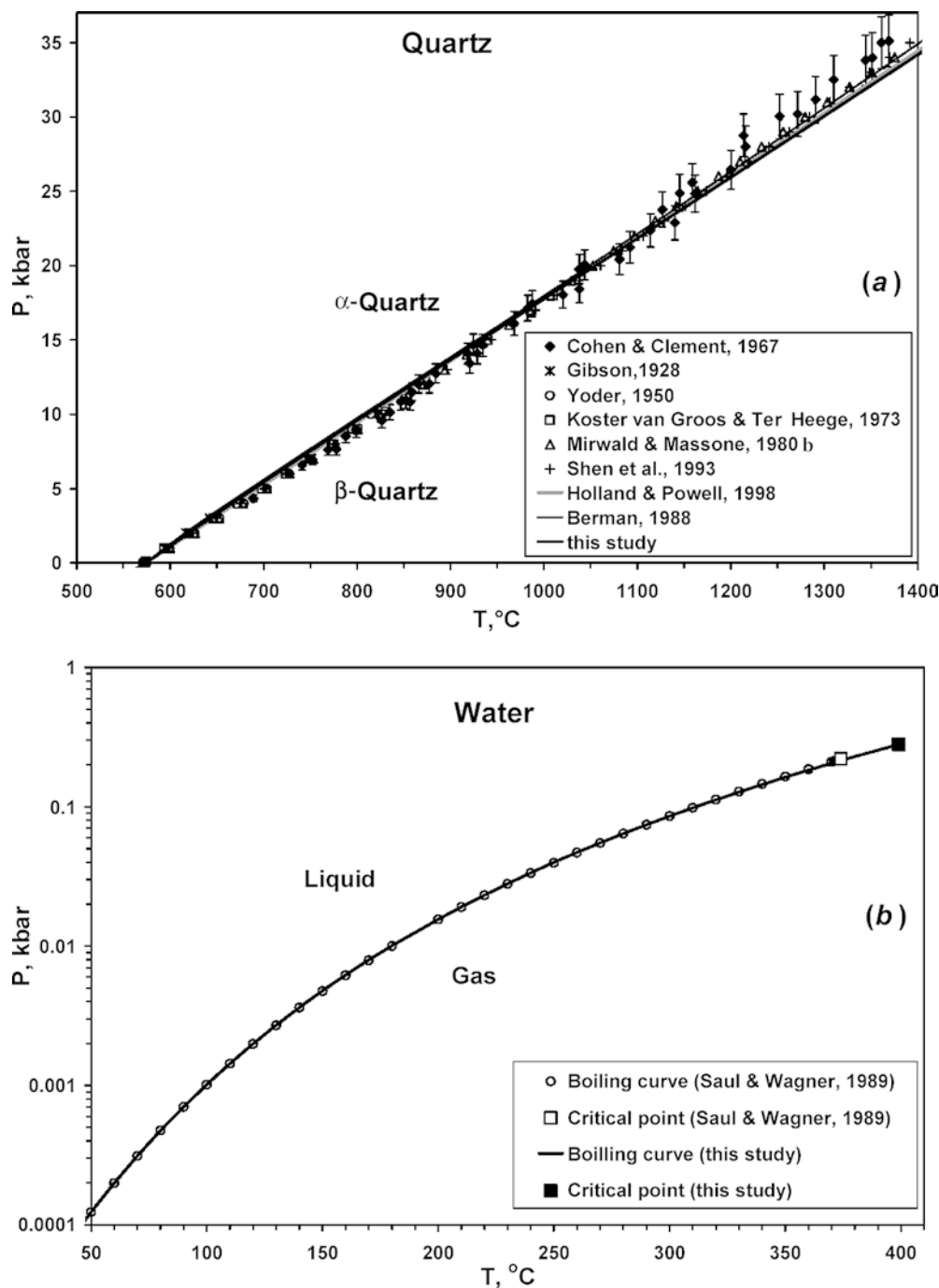
obtained for the α–β transition in quartz (Fig. 9a) and the liquid–gas transition in water (Fig. 9b), calculated with the use of Eqs. (20) and (30), respectively. Along the phase boundaries, mole fractions of the ordered/associated clusters (X_α / X_{Liq}) in the coexisting phases correspond to the conditions of equilibrium for both the internal "ordering" transition in each phase and the heterogeneous reaction between them. This is exemplified by Fig. 10, showing the Gibbs potential of quartz (Fig. 10a) and water (Fig. 10b) in the region of the phase transitions. Along these curves, two analogous minima occur in both cases, corresponding to the two stable phases differing in the degree of ordering/association. Figure 9 shows that the derived Gibbs energy equations allow an accurate description of experimental data. However, the critical point of water calculated using Eq. (30) appears to be 25 K higher than the experimentally determined datum (Fig 9b). This discrepancy is related to the difficulties discussed above in describing the continuous thermodynamic properties of fluid in the region of the critical point.
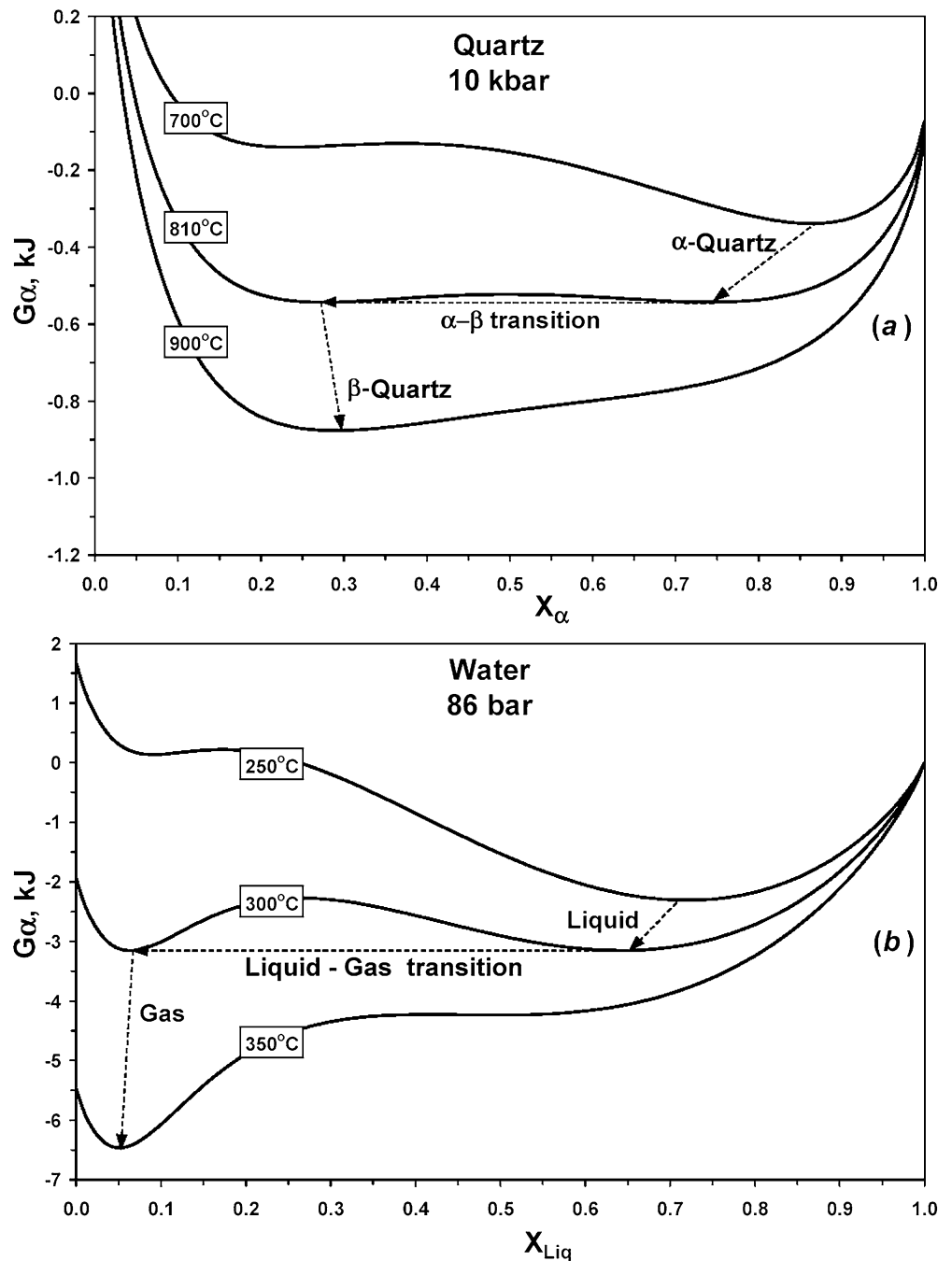
444

Figure 11 shows some mineral equilibria calculated using the data of Table 2. Comparison of the calculated phase boundaries with experimental data shows that the equations of Gibbs free energy derived here lead to accurate descriptions of the various phase boundaries, including the dehydration reaction brucite = periclase + water to very high pressures and temperatures (1250 °C, 150 kbar).

Discussion and conclusions

The equations for Gibbs free energy described here are sufficiently accurate to describe and extrapolate thermodynamic properties and phase equilibria on the basis of experimental data on isobaric heat capacity and molar volume. This implies that they can be effectively used in thermodynamic data bases of petrological interest. Moreover, they are relatively simple and lead to a uniformity of representation of the Gibbs potential as a direct function of P and T for very different phases (the software implementing the equations discussed in this paper for thermodynamic calculations is available by request from the corresponding author). It should be noted that the proposed model employs not more than 16 adjustable parameters. By comparison, the Helmholtz free energy equations that allow reasonable

Fig. 11a–c Comparison of selected calculated phase transitions in the system MgO–SiO$_2$–H$_2$O with the experimental data
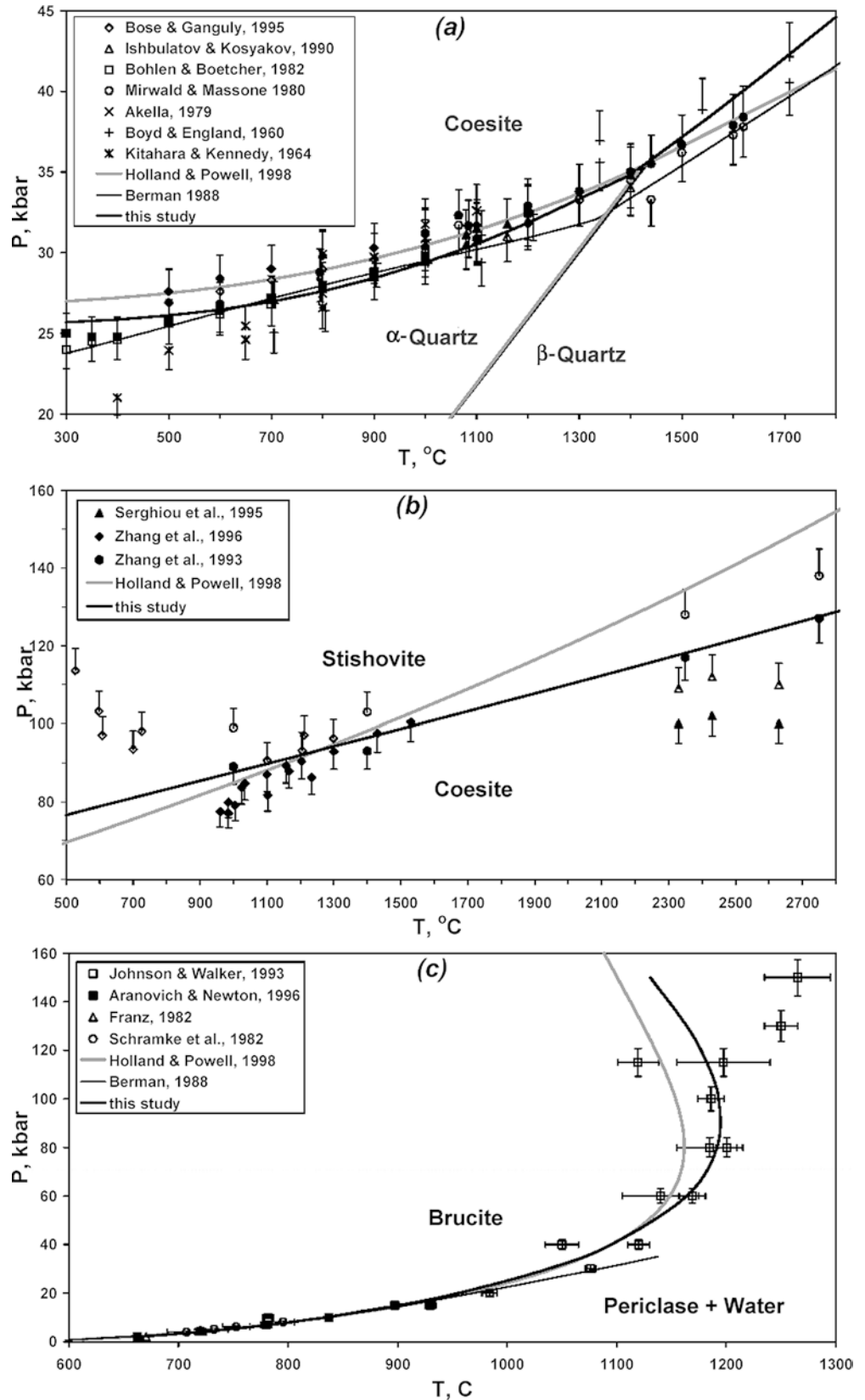
descriptions of a one-component fluids over a wide P–T range, including the two-phase region, normally contain 30–80 empirical parameters (e.g. Altunin 1975; Sychev et al. 1979; Saul and Wagner 1989; Stewart and Jacobson 1989; Hill 1990). The Gibbs free energy equation for quartz proposed by Dorogokupets (1995) for a

446
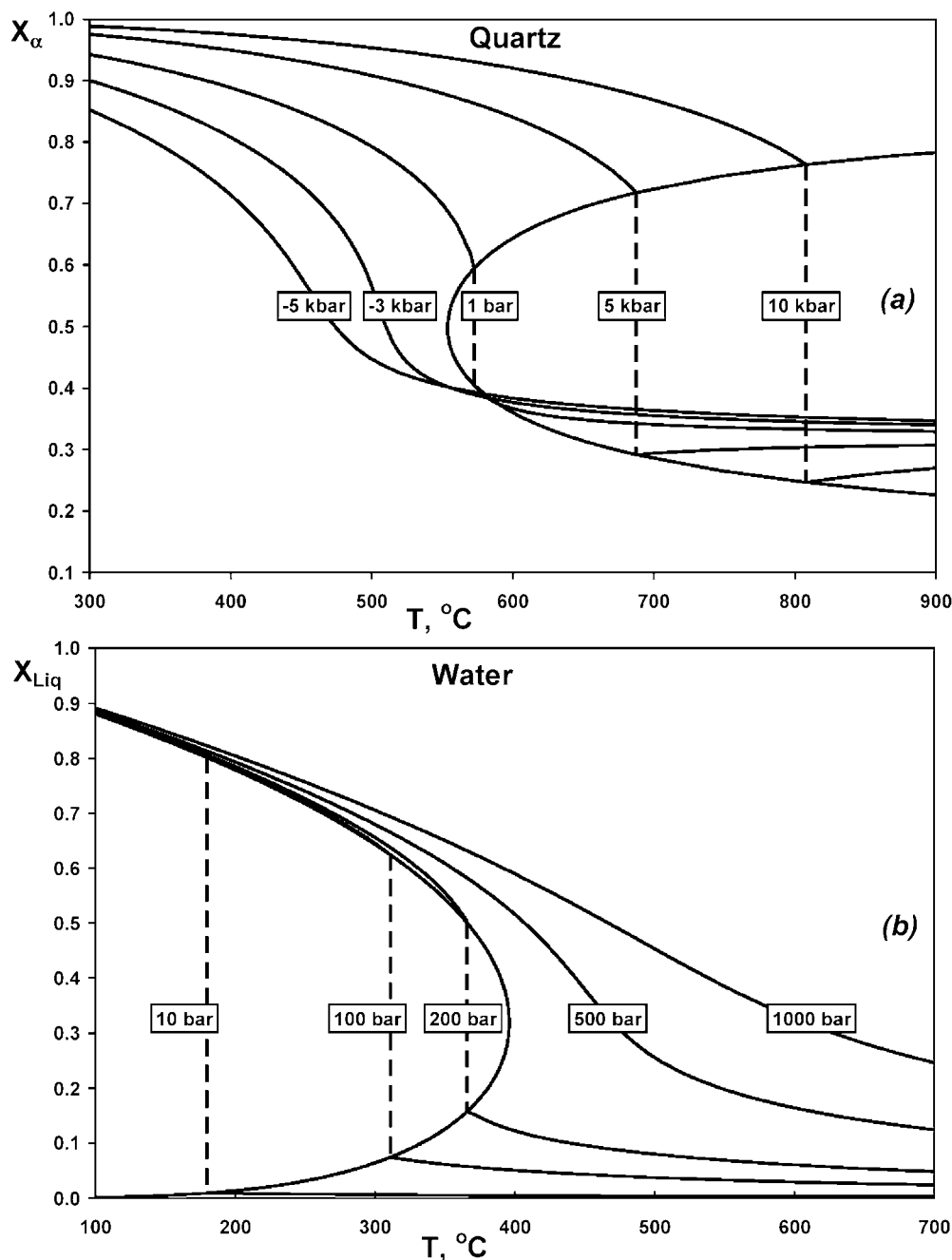
description of the λ-transition contains 26 parameters. In the case of simple phases, Equation (12) with 10–12 adjustable parameters allows an accurate description of the heat capacity and volume over a wide range of P–T conditions (20–3000 K, 0–800 kbar), including the important low-temperature (20–200 K) region relevant for correct representation of the third-law entropy according to Eq. (9a).

On the other hand, the approach presented here also leads to novel insights into the structure of crystalline phases with λ-transitions and fluids. The derived Gibbs free energy equations for such phases require the calculation of an equilibrium ordering parameter to satisfy Eqs.

(19) and (21), as illustrated by Fig. 10. Figure 12 shows the calculated P and T dependence of the ordering parameter for quartz (Fig.12a) and for water (Fig.12b). For quartz, the calculated miscibility gap widens with increasing pressure (the calculated critical point corresponds to $T = 553$ °C, $P = -880$ bar). A hypothetical homogeneous silica phase, with the ordering parameter X_α changing continuously with temperature, would exist below this point (Fig. 12a). These relationships are very similar to those in the aqueous fluid above the critical point (Fig. 12b). Accordingly, the heat capacity and coefficient of thermal expansion show maxima at the maximum value of the derivative $\partial X/\partial T$ (Figs. 13, 14).

Fig. 13a, b Isobars of the temperature dependence of isobaric heat capacities for quartz (**a**) and water (**b**)
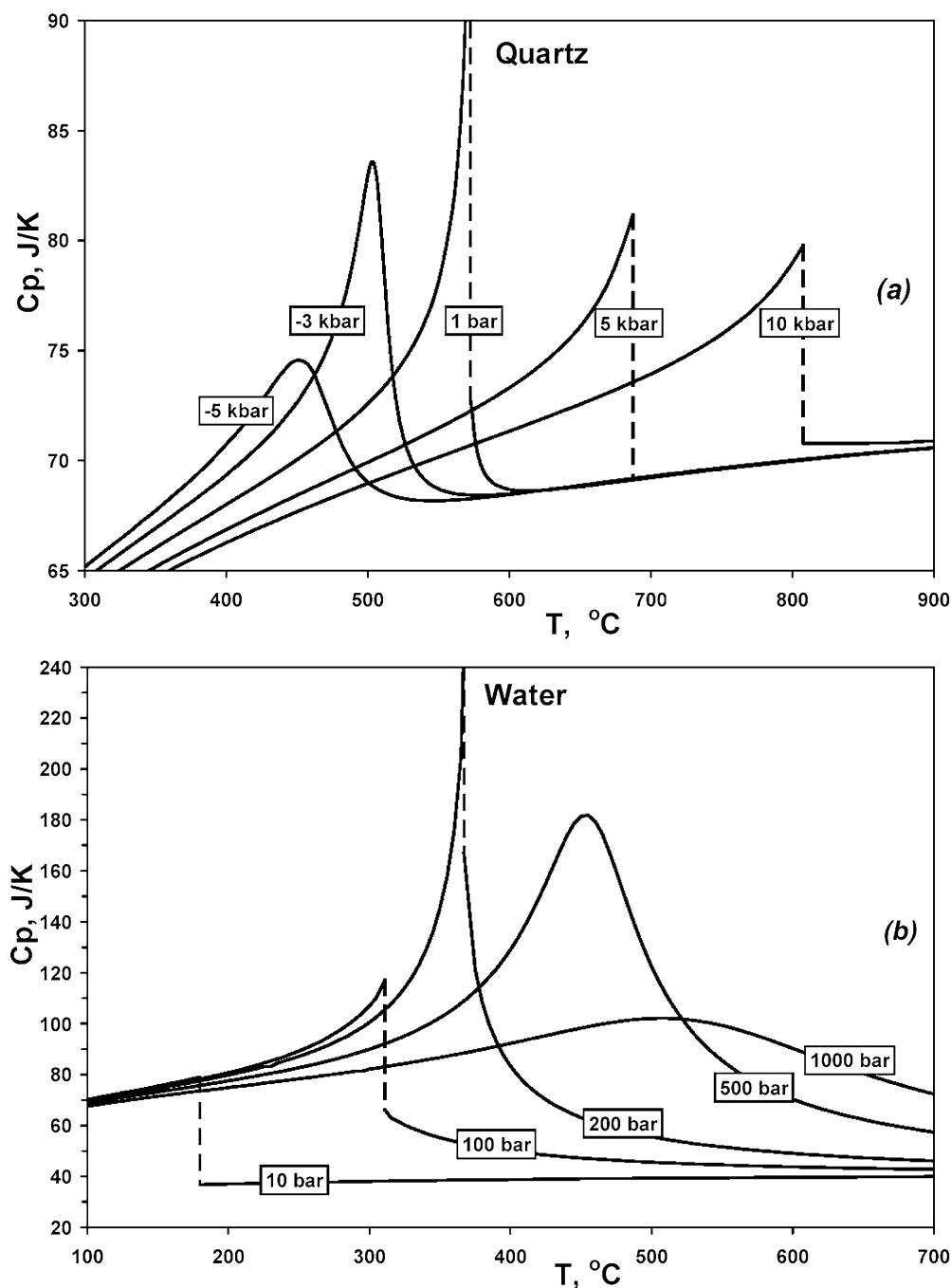
Comparison of the thermodynamic functions and ordering parameters of quartz and those of aqueous fluid (Figs. 13, 14) thus reveal a clear analogy, demonstrating the thermodynamic similarity of ordering phenomena in fluid and crystalline states (Landau and Lifshitz 1959). It should also be noted that the possible existence of a critical point for a crystalline substance with a λ-transition was predicted theoretically by Landau (e.g. Landau and Lifshitz 1959). Our test calculations have also shown that a similar thermodynamic approach can be applied to treat order/disorder transitions in binary alloys with pronounced λ-anomaly.

An important question concerns the physical meaning of the ordering parameters X_α and X_{Liq} used for the description of the Gibbs free energy of quartz and aqueous fluid, respectively. For both water and quartz, this parameter cannot be directly obtained from physical measurement, and therefore appears entirely abstract. However, a correspondence between X_{Liq} and the number of clusters follows from the similarity of Eqs. (22) and (24). Therefore, $X_{Gas} = 1 - X_{Liq}$ may be interpreted as an apparent mole fraction (thermodynamic probability) of the monomers, X_1, in the fluid, and X_{Liq} is the bulk mole fraction (thermodynamic

Fig. 14a, b Isobars of the temperature dependence of the coefficient of thermal expansion for quartz (**a**) and water (**b**)
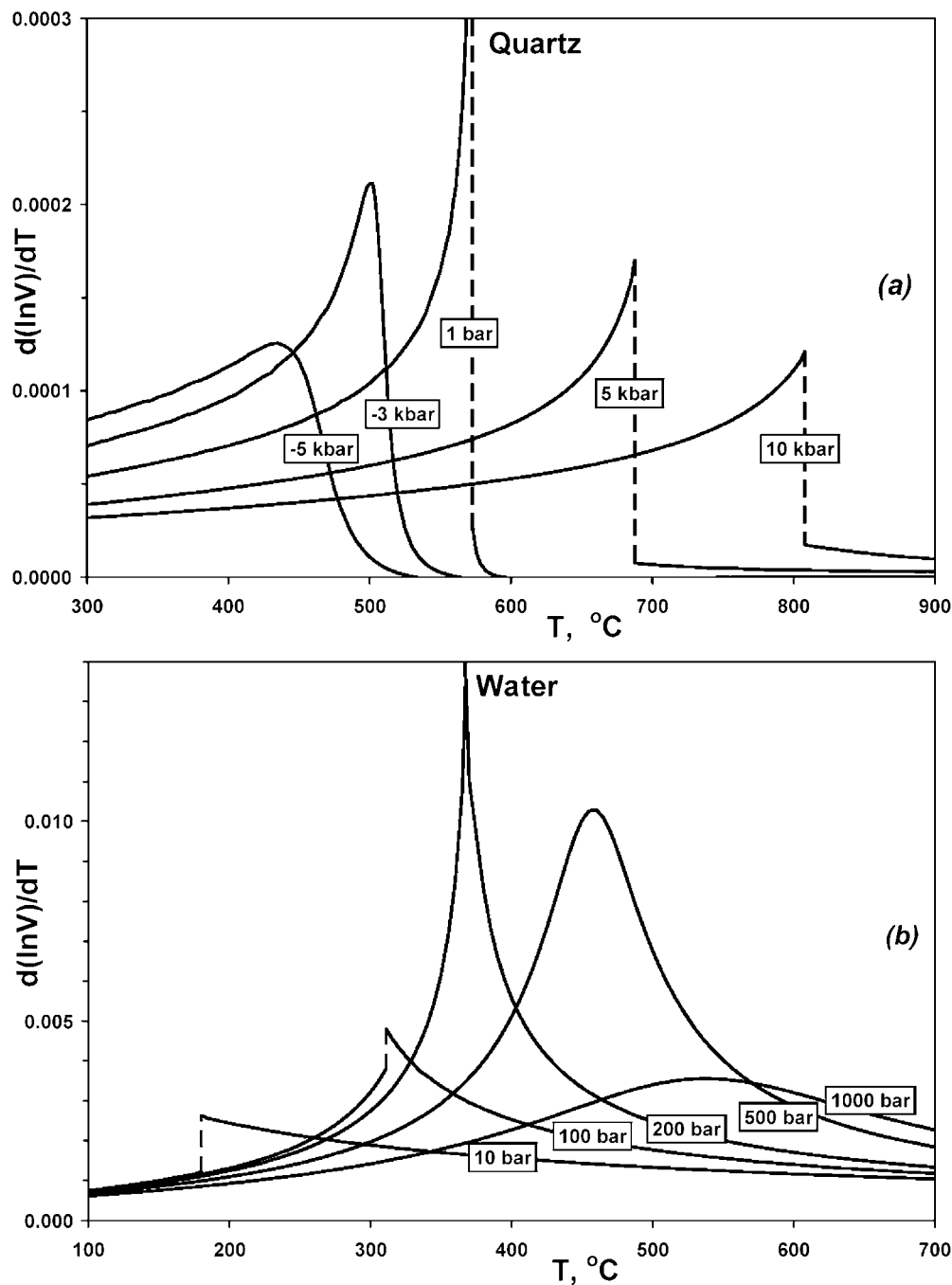
probability) of the clusters with $n \geq 2$. The concept of the existence of two distinct states of molecules in a fluid appears consistent with investigations of the water structure by Gorbaty and Demianets (1983), who demonstrated that the near-critical fluctuations are preserved at elevated P–T conditions above the critical point to a pressure of 1 kbar and temperatures of 500 °C. In the supercritical region, there are short-term space fluctuations that correspond to the liquid-like and gas-like states. Presence of clusters of water in the supercritical region is found in molecular dynamics experiments, even at densities of less than 0.2 gcm^{-3}

(Churakov and Kalinichev 1999), thus validating our thermodynamic formalism.

Further examples of the correspondence between the calculated ordering parameters and physical measurements are demonstrated in Fig. 15. Figure 15a presents the negative linear correlation of the estimated ordering parameter X_α with the sum of mean-squares displacements (MSD) of the oxygen atoms in the quartz structure, as determined for the λ-transition by Kihara (1990). The high correlation coefficient ($r = -0.987$) shows that the calculated decrease of X_α with increasing temperature reflects the real mechanism of disordering.

Fig. 15a–c Comparison of the ordering parameters with experimentally determined structural parameters for quartz (**a**) and water (**b**),(**c**) **a** A negative correlation ($r = -0.987$) between X_α and sum of mean-squares displacements (MSD) of oxygen atoms along axes 1–3 (Kihara 1990) at $P = 1$ bar and $T = 600–1100$ K. **b** A positive correlation ($r = 0.942$) between X_{Liq} and mole fraction of hydrogen bonds X_H (Gorbaty and Kalinichev 1995) at a $P = 1$ kbar and $T = 0–550$ °C. (**c**) A negative correlation ($r = -0.997$) between X_{Liq} and content of monomers N_M (mol%) (Luck 1980) in the liquid phase along the boiling curve
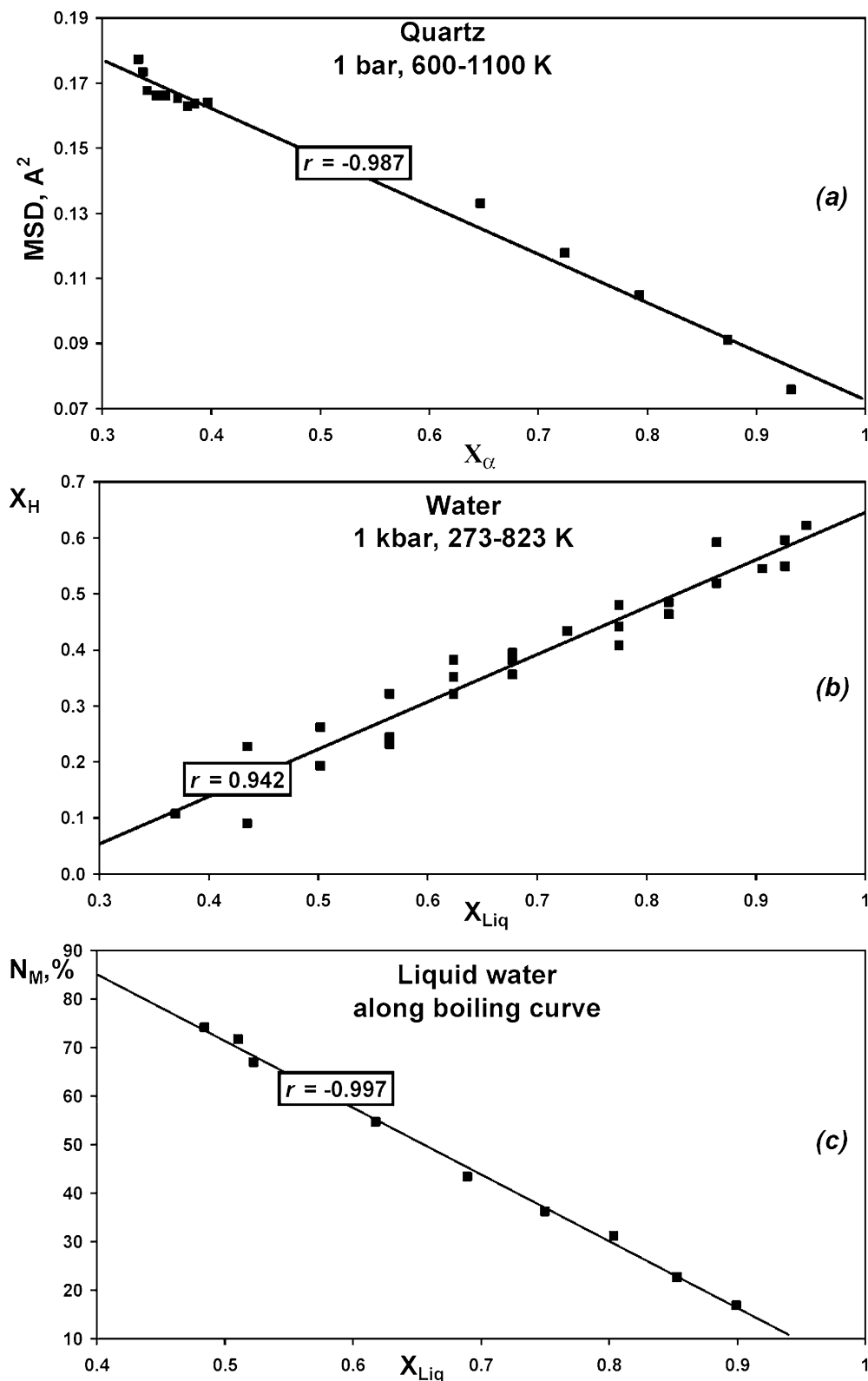
In Fig. 15b, the mole fraction of molecules in the liquid-like state X_{Liq} is compared to the mole fraction of hydrogen bonds X_H, calculated by Gorbaty and Kalinichev (1995) from experimental data (the association of molecules in an aqueous fluid is mainly determined by hydrogen bonds). Figure 14c presents a comparison of the mole fraction of molecules in the liquid-like state X_{Liq} with the mole percent of monomers N_M (Luck
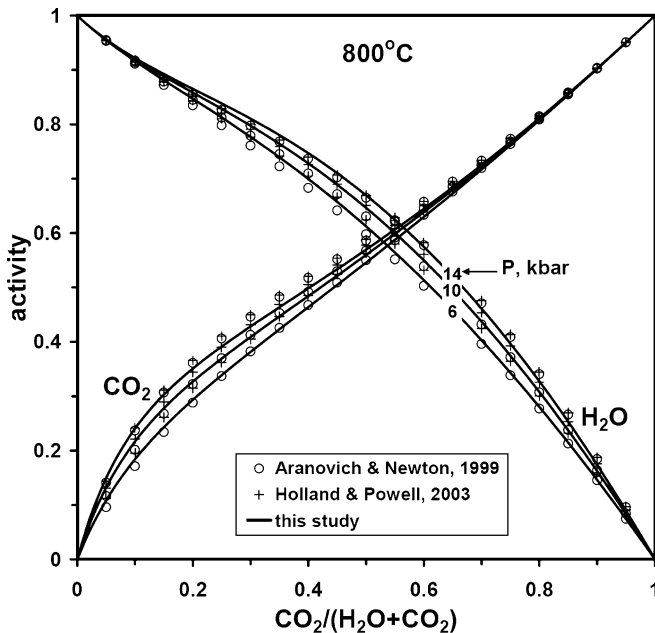
Fig. 16a–c Activity–composition plot for H_2O–CO_2 at 800 °C and 6–14 kbar calculated from eq. (27) with parameters linearly dependent on fluid composition (see text for discussion). Binary models of Aranovich and Newton (1999) and Holland and Powell (2003) are shown for comparison

1980). High coefficients of linear correlation between X_H and X_{Liq} ($r = 0.942$) and between N_M and X_{Liq} ($r = -0.997$) suggest that X_{Liq} quantitatively characterizes the degree of association of molecules in an aqueous fluid. Thus, it can be concluded that our relatively abstract ordering parameter reflects physical processes in minerals and fluids.

Figure 16 shows the results of modelling the mixing properties of an H_2O–CO_2 fluid with Eq. (27) and parameters linearly dependent on fluid composition, i.e. $B_{H_2O\text{-}CO_2} = B_{CO_2}X_{CO_2} + B_{H_2O}X_{H_2O}$, where $X_{CO_2} = CO_2/(CO_2 + H_2O)$, $X_{H_2O} = H_2O/(CO_2 + H_2O)$; $B_{H_2O\text{-}CO_2}$ are parameters of Eq. (27) for the binary fluid of given composition; B_{H_2O} and B_{CO_2} are, respectively, empirical parameters of Eq. (27) for pure H_2O (Table 2) and pure CO_2 ($\Delta H^{\circ}_{ord} = -20608.153$ J, $\Delta S^{\circ}_{ord} = -138.42315$ J/K, $\Delta C_P^{\circ}{}_{ord} = 10.0415201$ J/K, $W^H = -20859.049$ J, $W^S = 36.8658607$ J/K, $W^{Cp} = 0$, and $\phi = 6551.312$ bar, Gerya and Perchuk 1997). Our results coincide well with the empirical mixing models of Aranovich and Newton (1999) and Holland and Powell (2003) based on experimental data. This suggests that simple linear mixing rules can be used to extend our model on fluid mixtures without introducing any additional parameters. This also implies that non-ideality of mixing in multicomponent fluids is primarily related to changes in the degree of association of fluid molecules (X_{Liq}) with changing fluid composition, as directly accounted for by Eq. 27.

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Appendix 1. Derivation of Eq. (2)

The derivation of Eq. (2) follows standard logic of statistical mechanics (e.g. Hill 1956; Kubo 1965; Toda et al. 1992; Landau and Lifshitz 1959), but is based on an ensemble not treated in standard textbooks on statistical mechanics.

Let us first consider a substance in a condensed state, solid or liquid, at a relatively low temperature, when its atoms are close to each other and vibrate mainly around equilibrium positions. A system with N atoms will have $3N$ vibrational degrees of freedom, and, from the viewpoint of mechanics, can be referred to as a system of $3N$ independent quantum oscillators (e.g. Landau and Lifshitz 1959). The Gibbs free energy of a system of quantum oscillators in equilibrium at constant P and T can also be expressed with the P–T partition function (Toda et al. 1992)

$$G = -k_B T \ln(Y), \tag{A1}$$

$$Y = \sum_i \int_0^\infty \exp\{-[E_i(V) + PV]/k_B T\}\, dV \tag{A2}$$

where Y is the statistical sum over states, k_B is Boltzmann's constant, V is the system volume and $E_i(V)$ is the system energy for the i-th quantum state as a function of the volume. Theoretical expressions for $E_i(V)$ are

unavailable and empirical approximations are used instead. For integration of Eq. (A2) we take into account that at given P and T the fluctuation of volume of condensed substance is insignificant. If for an i-th state at a given P only one system volume $V_i(P)$ refers to a non-zero probability, then

$$\int_0^\infty \exp\{-[E_i(V) + PV]/k_B T\}\, dV = \exp[-H_i(P)/k_B T], \tag{A3}$$

where $H_i(P) = E_i(P) + PV_i(P)$ and $E_i(P) = E_i[V_i(P)]$.

$H_i(P)$, $E_i(P)$ and $V_i(P)$ are enthalpy (or, more specifically, its microscopic analogue), energy and volume of the system, respectively, in an i-th state as functions of P. If the apparent volume $V_i(P)$ and corresponding $H_i(P)$ and $E_i(P)$ in Eq. (A3) are valid for a case of the i-th quantum state at given P with insignificant fluctuations of the system volume V relative to $V_i(P)$, then Eq. (A2) can be simplified to

$$Y = \sum_i \exp[-H_i(P)/k_B T]. \tag{A4}$$

Equation (A4) differs from equations normally given in statistical mechanics (e.g. Hill 1956) in that the volume integral is taken before summation of the quantum states of the oscillators.

Normalizing the partition function relative to zero-point vibrations gives

$$G = G_0(P) - k_B T \ln(Y_0), \tag{A5}$$

where $Y_0 = \sum \exp[-\Delta H_i(P)/k_B T]$, $G_0 = H_0(P) - TS_0$, $\Delta H_i(P) = H_i(P) - H_0(P) = \Delta E_i(P) + P\Delta V_i(P)$, $H_0(P) = E_0(P) + PV_0(P)$, $\Delta E_i(P) = E_i(P) - E_0(P)$, $\Delta V_i(P) = V_i(P) - V_0(P)$. Y_0 is the statistical sum normalized relative to the state of zero-point vibrations. $G_0(P)$, $H_0(P)$, $E_0(P)$ and $V_0(P)$ are, respectively, the pressure-dependent Gibbs free energy, enthalpy, energy and volume of the system for the state of zero-point vibrations. S_0 is entropy of the system for the state of zero-point vibrations (in case of ordered crystalline phases, it is equal to zero according to Nernst's law). $\Delta H_i(P)$, $\Delta E_i(P)$ and $\Delta V_i(P)$ are, respectively, the pressure-dependent changes of enthalpy, energy and volume due to transition from the state of zero-point vibrations to the i-th quantum state. Taking into account 3N independent oscillators:

$$Y_0 = \prod_i^{3N} Y_{0i}, \tag{A6}$$

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

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

Y_{0i} is the statistical sum for the i-th oscillator normalized relative 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, respectively, pressure-dependent

changes in enthalpy, energy and volume due to transition of the i-th oscillator from the state of zero-point vibrations to the j-th energy level. To calculate Y_{0i}, it is assumed that every oscillator has an infinite number of energy levels and that $\Delta H_{ij}(P)$, $\Delta E_{ij}(P)$ and $\Delta V_{ij}(P)$ are proportional to j (e.g. Landau and Lifshitz 1959). Then

$$\Delta H_{ij}(P) = j\Delta H_{i0}(P), \tag{A7}$$

$$Y_{0i} = 1/\{1 - \exp[-\Delta H_{i0}(P)/k_B T]\}, \tag{A8}$$

$$\Delta H_{i0}(P) = \Delta E_{i0}(P) + \Delta V_{i0}(P). \tag{A9}$$

$$G = H_0(P) - TS_0 + k_B T \sum_i^{3N} \ln\{1 - \exp[-\Delta H_{i0}(P)/k_B T]\}, \tag{A10}$$

where $\Delta H_{i0}(P)$, $\Delta E_{i0}(P)$, and $\Delta V_{i0}(P)$ are, respectively, pressure-dependent changes in enthalpy, energy and volume due to transition of the i-th oscillator between neighbouring energy levels. The form of Eq. (A10) is similar to a standard equation for the Helmholtz free energy of the system of independent quantum oscillators (e.g. Landau and Lifshitz 1959; Kubo 1965; Toda et al. 1992), and the only difference is that the statistical sum over states is expressed in terms of enthalpy changes (not energy changes) related to the transitions of the oscillators.

If $N = \nu N_A$ (N_A is Avogadro's number, ν is the number of atoms in a substance molecule) and functions $\Delta H_{i0}(P)$ have similar values for n big groups of oscillators, then Eq. (A9) can be rewritten in the form of Eq. (2)

Appendix 2. Derivation of Eq. (16)

The derivation of Eq. (16) is also based on the P–T partition function (Toda et al. 1992) and follows the same logic as the derivation of Eq. 2 (see Appendix 1).

If the λ-transition leads to notable changes in the thermal vibrations of atoms, this must be taken into account in a description of the energy transitions of oscillators; i.e. G_s in Eq. (2) depends on X_α. Suppose that for a certain oscillator energy level m, whose energy depends on X_α, the enthalpy effect of the transition ΔH_{si} changes. Then, the statistical sums Y_{0i} in Eq. (A6) take the form

$$\begin{aligned} Y_{0i} = &\{[1 - \exp(-\Delta H_{i\beta}/k_B T)] + \exp(-\Delta H_{i\lambda}/k_B T) \\ &\times [\exp(-\Delta H_{i\beta}/k_B T) - \exp(-\Delta H_{i\alpha}/k_B T)]\}/ \\ &\{[1 - \exp(-\Delta H_{i\alpha}/k_B T)] \cdot [1 - \exp(-\Delta H_{i\beta}/k_B T)]\}, \end{aligned} \tag{A11}$$

where $\Delta H_{i\alpha}$ is the enthalpy change of the energy transitions (ΔH_{i0}) beginning with the zero level to the level (m-1) in the ordered phase, $\Delta H_{i\beta}$ is the enthalpy change of the energy transitions beginning with the level m in the disordered phase, $\Delta H_{i\lambda}$ is the enthalpy change of the transition from the zero level to the level m as a function of X_α and can be expressed by a power series expansion:

$$\Delta H_{i\lambda} = \sum_{k=0}^{u} \Delta H_{i\lambda k}(X_\alpha)^k, \tag{A12}$$

where $\Delta H_{i\lambda k}$ denotes the expansion coefficients. Then Eq. (A10) can be transformed to:

$$\begin{aligned} G_s = &H_s - TS_s^o + \sum_{i=1}^{n} c_i RT \ln\{(1 - e_{\alpha i})(1 - e_{\beta i})/[(1 - e_{\beta i}) \\ &+ e_{\lambda i}(e_{\beta i} - e_{\alpha i})]\}, \end{aligned} \tag{A13}$$

where $e_{\alpha i} = \exp(-\Delta H_{si\alpha}/RT)$, $e_{\beta i} = \exp(-\Delta H_{si\beta}/RT)$, $e_{\lambda i} = \exp(-\Delta H_{si\lambda}/RT)$, $e_{oi} = \exp(-\Delta H_{si\alpha}^\circ/R T_o)$, $\Delta H_{si\alpha} = \Delta H_{si\alpha}^\circ + \Delta V_{si\alpha}^\circ \Psi$, $\Delta H_{si\beta} = \Delta H_{si\beta}^\circ + \Delta V_{si\beta}^\circ \Psi$, and $\Delta H_{si\lambda} = \sum_{k=0}^{u} (\Delta H_{si\lambda k}^\circ + \Delta V_{si\lambda k}^\circ \Psi)(X_\alpha)^k$.

$\Delta H_{si\alpha}$, $\Delta H_{si\beta}$, and $\Delta H_{si\lambda}$ are values of $\Delta H_{i\alpha}$, $\Delta H_{i\beta}$ and $\Delta H_{i\lambda}$ taken for N_A oscillators. Equation (16) is derived from Eq. (A13) by using $u = 2$, $n \leq 5$ and Eqs. (5)–(6).

Appendix 3. Derivation of Eq. (27)

The last two terms in Eq. (26) can be expressed as

$$-X_{Gas}\Delta G_{ord}^o + G^e = G_P + G_T, \tag{A14}$$

where $G_P = \int_{Po}^{P}(-\Delta V_{ord}^o X_{Gas} - V^e)dP$, and $G_T = -X_{Gas}(\Delta H_{ord}^o - T\Delta S_{ord}^o) + H^e - TS^e + \int_{T_o}^{T}[-\Delta C_P^o(T)_{ord} X_{Gas} + C_P^e(T)]dT - T\int_{T_o}^{T}[(-\Delta C_P^o(T)_{ord}X_{Gas} + C_P^e(T))/T]dT$.

ΔV_{ord}^o and V^e are the standard volume change of short-term "ordering" transition 25 (Gas = Liq) and the excess volume of the fluid, respectively, both being functions of P and T, ΔH_{ord}^o and ΔS_{ord}^o are the standard enthalpy and entropy changes of Reaction (25) at P_o and T_o, H^e and S^e are, respectively, contributions to excess enthalpy and entropy not related to V^e at P_o and T_o, $\Delta C_P^o(T)_{ord}$ and $C_P^e(T)$ are, respectively, the standard heat capacity change of "ordering" transition (25) and the excess heat capacity of the fluid, both dependent on temperature at P_o.

To quantify G_P from Eq. (A14) it can be assumed that the volume of a phase that contains only molecules in the gas-like (free) state can be expressed as two terms, namely, the conventional volume of the molecules V_s and the free volume V_f (Prigogine and Defay 1954). Then

$$V_{Gas}^o = V_s + V_f = V_s + RT/P. \tag{A15}$$

The volume of one mole of a substance that contains only molecules in the liquid-like (associated) state is solely determined by the conventional volume of the molecules

$$V_{Liq}^o = V_s. \tag{A16}$$

Hence, the standard volume change of Reaction (25) is $\Delta V_{ord}^o = V_{Liq}^o - V_{Gas}^o = -RT/P$.

Considering Eqs. (A15) and (A16), the total volume V of a mixture consisting of molecules in both the liquid-like and the gas-like states

$$V = X_{Gas}V_{Gas}^o + X_{Liq}V_{Liq}^o - V^e = V_s - X_{Gas}\Delta V_{ord}^o - V^e$$
$$= V_s + X_{Gas}RT/P - V^e. \qquad (A17)$$

The negative sign of V^e corresponds to a decrease in the free volume V_f caused by attraction between molecules of any type. Then, in line with the van der Waals equation

$$P = RT/(V - \beta) - \phi_a,$$

where β is the correction for molecular volume, i.e. $\beta = V_s$, and $\phi_a = const/V^2$ is the correction for the attractive interaction between the molecules. Equation (A17) can be rewritten as

$$V = V_s + X_{Gas}RT/P - V^e = V_s + X_{Gas}RT/(P + \phi_a). \qquad (A18)$$

Apparently, ϕ_a depends on the average distance between molecules in a fluid. Taking into account the volume change of Reaction (25), this distance is a function of X_{Liq}. As the external pressure decreases, the volume of the system approaches that of the ideal gas, RT/P, and both X_{Liq} and ϕ_a tend to zero. As the pressure increases, X_{Liq} and ϕ_a also increase. Hence, ϕ_a can be expressed as a function of X_{Liq} in the form

$$\phi_a = \phi_{a1}X_{Liq} + \phi_{a2}X_{Liq}^2 + \cdots + \phi_{aq}X_{Liq}^q, \qquad (A19)$$

where $\phi_{a1}, \phi_{a2}, \ldots$, and ϕ_{aq} are coefficients independent of X_{Liq}. Evidently, with X_{Liq} approaching 1, ϕ_a approaches ϕ (Eq. 5), because both corrections characterize the same attractive interaction between molecules. Then, in accordance with Eq. (A19)

$$\phi = \phi_{a1} + \phi_{a2} + \cdots + \phi_{aq}. \qquad (A20)$$

For a transition from the liquid-like state to the gas-like one, when distances between the molecules increase significantly, Eqs. (A18)–(A19) provide an additional correction for the attractive interaction. Taking for the standard state $\phi_a = 0$, integration of Eq. (A17) in accordance with Eq. (A14) yields the following equation for G_P

$$G_P = X_{Gas}RT \ln[(P + \phi_a)/P_o], \qquad (A21)$$

where $\phi_a = \phi_{a1}X_{Liq} + \phi_{a2}X_{Liq}^2 + \cdots + \phi_{aq}X_{Liq}^q$.

Using the Margules expansion to express the integral excess Gibbs free energy of mixing of liquid-like and gas-like molecules in a fluid and assuming $\Delta C_{Pord}^o(T)$ and $C_P^e(T)$ constant, G_T in Eq. (A14) can be defined as

$$G_T = -X_{Gas}\{\Delta H_{ord}^o - T\Delta S_{ord}^o + \Delta C_{Pord}^o[T - T_o$$
$$- T\ln(T/T_o)]\} + \sum_{j=1}^m W_j^G X_{Gas}X_{Liq}^j, \qquad (A22)$$

where $W_j^G = W_j^H - TW_j^S + W_j^{Cp}[T - T_o - T\ln(T/T_o)]$.

C_{Pord}^o is the standard heat capacity effect of Reaction (25) at P_o and T_o, and the Ws are the Margules parameters.

Equation (27) is derived from Eqs. (A14), (A21) and (A22) using $q = 2$, $m = 1$ and $X_{Gas} + X_{Liq} = 1$.