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THE RELIABILITY OF THERMODYNAMIC CALCULATIONS ON CHEMICAL AND PHASE EQUILIBRIA AT ULTRAHIGH PRESSURES*

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A comparison is made of semiempirical methods of constructing thermal equations of state for solids. It is found that isothermal P-V curves and $\int_0^P V dP$ are sensitive to the method used in the construction, and estimates are made of the random errors. It is shown that isotherms agree with one another to within 7% in pressure in the megabar region as calculated by the potential method and from the theory of elasticity, which corresponds with the errors of current methods of static and shock compression.

The calculations show that the numerical values of $\int_0^P V dP$ are determined with high accuracy (never less than 1-2%) and can be tabulated in thermodynamic handbooks along with the standard thermodynamic functions. Because monovariant curves for chemical and phase equilibria at ultrahigh P and T are based on the determination of $\int_0^P V dP$, the reliability of such calculations has a rigorous basis. Basic thermodynamic specifications are formulated for calculations of chemical and phase equlibria over wide ranges in pressure and temperature.

Research on the internal structure and chemical evolution of the planet is a central task in Earth sciences. Many aspects of this fundamental problem do not allow of direct solution by means of observation or model experiments. Theoretical and experimental geophysics are concerned with the composition of the mantle, the Earth's thermal history, the processes resulting in the core, and so on. The advances made in this area are well known [1-3].

At the same time, study of the physicochemical and geochemical features of the processes that have occurred and are occurring deep within the Earth has not been common. It is clear that further research on the structure and composition of deep parts of the Earth should be based on geochemical methods and the use of rigorous techniques from chemical thermodynamics along with experimental information on the physicochemical properties of the Earth's material, which enable us to examine the directions taken by chemical reactions and to construct phase diagrams for mineral systems at the temperatures and pressures found deep within the Earth [4].

A basic problem here is the reliable determination of the free energy of reaction $\Delta G(P, T)$. One of the major conditions is correct determination of $\int_0^P V dP$ for minerals. This also will be considered here.

BASIC SPECIFICATIONS FOR INFORMATION ON EQUATIONS OF STATE REQUIRED IN THERMODYNAMIC CALCULATIONS ON CHEMICAL AND PHASE EQUILIBRIA OVER WIDE RANGES IN PRESSURE AND TEMPERATURE

The free energy ΔG_T^P of a chemical transformation at arbitrary P and T can be calculated by means of a thermodynamic equation:

$$\Delta G_T^P = \Delta G_T^0 + \int_0^P \Delta V \, dP, \tag{1}$$

where ΔG_T^0 is the change in the standard free energy and ΔV is the volume change at given P and T.

Clearly, to study reactions deep within the Earth at pressures of hundreds and thousands of kilobars it is necessary to know the relationship between volume, temperature, and pressure, i.e., the equation of state. Such equations can be used with experimental data on the standard thermodynamic functions to calculate the $P-T$ parameters of equilibria in a mineral system throughout the relevant temperature and pressure ranges, while experimental $P-T$ curves for monovariant equilibria give a thermodynamically rigorous derivation of standard free energies inaccessible to direct calorimetric determination, as well as other characteristics of chemical reactions involving high-pressure and low-pressure phases [5].

Therefore, equations of state are a major link in constructing a system of mutually consistent thermodynamic parameters for minerals.

Measurements and calculations of standard thermodynamic functions involve certain specifications for the experimental methods, and also for consistency in the constants, accuracy in the calculations, and evaluation of the corresponding errors [6, 7]. This enables us to tabulate thermodynamic constants. Thermodynamic functions such as enthalpy, entropy, and free energy constitute a system of related quantities: $\Delta G = \Delta H - T\Delta S$.

Clearly, the choice of key quantities acquires particular significance in preparing fundamental reference works that survey the accumulated experimental data; a very important requirement here is internal consistency in the tabulated values [6].

During the last decade, there have been advances in experimental and theoretical researches on the chemistry, physics, and geophysics of high pressures [1, 3, 4, 8-10]. A unique apparatus has been built in which static pressures of over 1 mbar and dynamic ones up to 10 mbar or above can be attained. It has become possible to perform direct synthesis and decomposition of minerals

in the transition zone and lower mantle, with measurements of the compressibilities and construction of equations of state. There have also been rapid abundances in the thermodynamics of reactions at high pressures and temperatures [4, 8].

Therefore, we now have extensive experimental evidence on simple systems, which can be used in physicochemical simulation. In that approach there are additional difficulties (as compared to thermodynamic calculations at atmospheric pressure) that are related to construction of equations of state, calculation of the integrals $\int_0^P V dP$, and selection and matching of the experimental data, which ultimately all influence the accuracy in calculating the free energy of reaction ΔG_T^P and the P-T curves for monovariant equilibria.

However, so far no criteria have been laid down for such calculations that enable us to evaluate the reliability and accuracy of the thermodynamic information at high pressures $\int_0^P V dP, \Delta G_T^P$, etc.). The following basic specifications for information on equations of state can be drawn up from the existing experience with thermodynamic calculations on chemical and phase equilibria at high pressures and temperatures [4, 5, 11]:

1. To calculate the P-T curves for chemical and phase equilibria at high pressures and temperatures we need information on the equations of state for the substances in the form of $\int_0^P V dP$. This must be available in a convenient practical form. The values of $\int_0^P V dP$ characterize the isothermal dependence of the chemical potential on pressure, and these values are of reference character, and should be tabulated in thermodynamic handbooks along with the standard thermodynamic functions.

2. The numerical values of $\int_0^P V dP$ for simple substances and compounds should be reliable. Within the limits of error they should be independent of the model and the method of constructing the equation of state.

3. Experiment provides the factual basis for constructing an equation of state. The experimental data on compressibility can be represented as compression curves (isotherms or shock adiabatics) or as elastic constants (adiabatic and isothermal compression moduli of various orders) under standard conditions. The latter in essence are differential characteristics of the compression curves and contain in concentrated form all the necessary information on the compressibility. For this reason the processing and matching of experimental compressibility data is best done at the level of elastic constants, in accordance with the specifications laid down for reference thermodynamic data. It is necessary to set up a data bank on the elastic, thermal, and caloric characteristics of substances.

4. Special consideration is needed of the sensitivity of the results to errors in the initial data. Reliability evaluation of thermodynamic calculations for high temperatures and pressures is very closely related to consistency in the primary experimental data and to comprehensive analysis of the random and systematic errors for all types of data.

5. Experiments to determine the elastic constants of various substances have not managed to satisfy the increasing demand for new data on low-pressure and high-pressure phases. For this reason, extensive use should be made of various methods of comparative calculation for elastic constants on the basis of the correlations in a series of compounds similar in composition and structure. The limits to the applicability of the methods and the accuracy of the results must be strictly defined.

Detailed information is required on the P-V-T properties and on the thermal, elastic, and caloric characteristics of substances over wide ranges in temperature and pressure in order to solve various problems in physicochemical simulation for endogenous processes (compression moduli of various orders, specific heat, entropy, thermal expansion coefficient, etc.).

In such calculations, particular attention must be given to the reliability and accuracy of the values of $\int_0^P V dP$, so here we shall analyze the reliability in determining these and the sensitivity of the values to ways of constructing the equations of state, and we also shall give a quantitative evaluation of the calculation errors.

SEMIEMPIRICAL MODELS FOR THERMAL EQUATIONS OF STATE FOR SOLIDS

It is impossible at present to construct an equation of state theoretically by analyzing the microscopic structure of the material and the character of the atomic interactions for any complicated compound. For this reason, various semiempirical approaches are widely used [1, 5, 9, 12-19].

There have been numerous special studies [1, 12, 14-16, 20] on the accuracy of semiempirical equations of state, but we are still far from a final decision. The criterion here is agreement with the experimental compressibility data. However, information on the compressibility is extremely restricted or entirely lacking for many geochemically important substances. Under these conditions, the prediction reliability criterion may be agreement between the equations of state derived from independent approximations.

Within the framework of semiempirical methods there are approaches based on concepts from the theory of elasticity and statistical solid-state physics. Let us consider the essentials of the commonest methods.

CONSTRUCTION OF AN EQUATION OF STATE FOR A SOLID BY ELASTIC-THEORY METHODS

Approaches in the theory of elasticity [20-23] to the construction of equations of state for solids are usually based on expanding the Helmholtz free energy $F(V, T)$ at constant temperature T_0 as a Taylor series in powers of the deformations with respect to some reference state* with voluem V_0:

$$F(V, T_0) = F(V_0, T_0) + \frac{\partial F}{\partial \varepsilon}\bigg|_{V_0, T_0} \varepsilon + \frac{1}{2} \frac{\partial^2 F}{\partial \varepsilon^2}\bigg|_{V_0, T_0} \varepsilon^2 + \frac{1}{6} \frac{\partial^3 F}{\partial \varepsilon^3}\bigg|_{V_0, T_0} \varepsilon^3 + \cdots, \tag{2}$$

where $\varepsilon = \varepsilon(V/V_0)$ is a measure of the deformation, with $\varepsilon(1) = 0$. One usually restricts oneself to the first few terms. Such finite expansions have an exact asymptotic meaning for small deformations. The exponent in the last term incorporated defines the order of the corresponding equation of state, which is readily derived by differentiating (2) with respect to the volume, since

$$P(V, T) = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial \varepsilon}\right)_T \frac{\partial \varepsilon}{\partial V} . \tag{3}$$

We also use a definition of the isothermal bulk modulus and the derivative of this with respect to pressure

$$K_T = -V\left(\frac{\partial P}{dV}\right)_T, \quad K_T' = \left(\frac{\partial K_T}{\partial P}\right)_T \tag{4}$$

and express the derivatives with respect to deformation in terms of the derivatives with respect to volume, which gives us the following relations for the first three coefficients in (2):

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*Here and subsequently the quantities with subscript 0 relate to the reference state. Usually, the reference state is chosen such that $P(V_0, T_0) = 0$.

$$\frac{\partial F}{\partial \varepsilon}\bigg|_{V_0,T_0} = -P\frac{\partial V}{\partial \varepsilon}\bigg|_{V_0,T_0}, \tag{5}$$

$$\frac{\partial^2 F}{\partial \varepsilon^2}\bigg|_{V_0,T_0} = \left[\frac{K_T}{V}\left(\frac{\partial V}{\partial \varepsilon}\right)^2 - P\frac{\partial^2 V}{\partial \varepsilon^2}\right]\bigg|_{V_0,T_0}, \tag{6}$$

$$\frac{\partial^3 F}{\partial \varepsilon^3}\bigg|_{V_0,T_0} = \left[-\frac{(K_T'+1)K_T}{V^2}\left(\frac{\partial V}{\partial \varepsilon}\right)^3 + \frac{3K_T}{V}\frac{\partial V}{\partial \varepsilon}\frac{\partial^2 V}{\partial \varepsilon^2} - P\frac{\partial^3 V}{\partial \varepsilon^3}\right]\bigg|_{V_0,T_0}. \tag{7}$$

In the theory of elasticity, which operates with macroscopic concepts and does not contain concepts such as "atom," "lattice," and so on, the question of what is meant by the deformation measure is important. It is familiar that the choice of deformation measure is ambiguous in the nonhydrostatic deformation of a solid [21-23]. The corresponding difficulties persist also in the hydro-static theory of isotropic and cubic bodies if we use finite expansions of the type of (2) in constructing the equation of state.

Proper choice of the deformation measure enables us to accelerate the con-vergence of the series of (2). Equations of state constructed from different deformation measures containing infinite numbers of terms are equivalent, but finite expansions with identical numbers of terms give different results.

Therefore, the accuracy of an equation of state is dependent on the number of terms in (2) and on the choice of deformation measure, and it is determined from the agreement between the theoretical curves and experimental data.

We may illustrate the difficulties arising here on the following example. Let the reference state be unstressed, i.e., $\partial F/\partial V|_{V_0, T_0} = 0$. We take the very simple deformation measure $\varepsilon = (V-V_0)/V_0$ and retain terms up to the third order in (2) to get

$$F(V, T_0) - F(V_0, T_0) = a_2\varepsilon^2 + a_3\varepsilon^3, \tag{8}$$

where

$$a_2 = \frac{1}{2}\frac{\partial^2 F}{\partial \varepsilon^2}\bigg|_{V_0,T_0}, \quad a_3 = \frac{1}{6}\frac{\partial^3 F}{\partial \varepsilon^3}\bigg|_{V_0,T_0}.$$

We substitute (8) into (3) to get

$$-P = \left(\frac{\partial F}{\partial \varepsilon}\right)_T\frac{\partial \varepsilon}{\partial V} = \frac{1}{V_0}(2a_2\varepsilon + 3a_3\varepsilon^2). \tag{9}$$

It is readily seen that the body obeying equation of state (9) can be compressed to a point by performing a finite amount of work. Therefore, equation (9) gives unsatisfactory results at large deformations.

Let us now consider some approaches to constructing the equation of state for a solid based on particular methods of choosing the deformation measure*.

The Lagrange approach through the description of deformations in an elastic body has a certain universality in the nonhydrostatic case [21] and gives the following expression for the deformation measure [17, 18]:

$$\varepsilon_L = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{2}{3}} - 1\right]. \tag{10}$$

In that case, formulas (5)-(7) for the coefficients in (2) can be transformed to

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*Particular interest attaches to deformation measures that can be extended directly to the nonhydrostatic case, since for most crystals we cannot apply the model of isotropic re-sponse to a hydrostatic stress. On the other hand, much attention is now being given to nonhy-drostatically stressed systems [24, 25].

$$\left.\frac{\partial F}{\partial \varepsilon_L}\right|_{V_0,T_0} = -3V_0 P(V_0, T_0), \tag{11}$$

$$\left.\frac{\partial^2 F}{\partial \varepsilon_L^2}\right|_{V_0,T_0} = -3V(-3K_T + P)|_{V_0,T_0} \tag{12}$$

$$\left.\frac{\partial^3 F}{\partial \varepsilon_L^3}\right|_{V_0,T_0} = -3V(9K_T K_T' - P)|_{V_0,T_0}. \tag{13}$$

The corresponding third-order equation of state is written as follows [18]:

$$P(\varepsilon_L, T_0) = -\frac{(1 + 2\varepsilon_L)^{-\frac{1}{2}}}{3V_0}(b_0 + b_1\varepsilon_L + b_2\varepsilon_L^2), \tag{14}$$

where

$$b_0 = \left.\frac{\partial F}{\partial \varepsilon_L}\right|_{V_0,T_0}, \quad b_1 = \left.\frac{\partial^2 F}{\partial \varepsilon_L^2}\right|_{V_0,T_0}, \quad b_2 = \frac{1}{2}\left.\frac{\partial^3 F}{\partial \varepsilon_L^3}\right|_{V_0,T_0}.$$

Equation of state (14) has the same disadvantages as (9). A check on the applicability to real substances has shown that it is unsatisfactory at high pressures ($P \geqslant 200$ kbar).

The Euler approach to describing deformations in an elastic body gives the following expression for the deformation measures [17, 18]:

$$\varepsilon_E = \frac{1}{2}\left[1 - \left(\frac{V}{V_0}\right)^{-\frac{2}{3}}\right]. \tag{15}$$

Then (5)-(7) can [18] be put as

$$\left.\frac{\partial F}{\partial \varepsilon_E}\right|_{V_0,T_0} = -3V_0 P(V_0, T_0), \tag{16}$$

$$\left.\frac{\partial^2 F}{\partial \varepsilon_E^2}\right|_{V_0,T_0} = -3V(-3K_T + 5P)|_{V_0,T_0}, \tag{17}$$

$$\left.\frac{\partial^3 F}{\partial \varepsilon_E^3}\right|_{V_0,T_0} = -3V[9K_T(K_T' - 4) + 35P]|_{V_0,T_0}. \tag{18}$$

Then the third-order equation of state takes the form [18]

$$P(\varepsilon_E, T_0) = -\frac{(1 - 2\varepsilon_E)^{\frac{5}{2}}}{3V_0}(c_0 + c_1\varepsilon_E + c_2\varepsilon_E^2), \tag{19}$$

where

$$c_0 = \left.\frac{\partial F}{\partial \varepsilon_E}\right|_{V_0,T_0}, \quad c_1 = \left.\frac{\partial^2 F}{\partial \varepsilon_E^2}\right|_{V_0,T_0}, \quad c_2 = \frac{1}{2}\left.\frac{\partial^3 F}{\partial \varepsilon_E^3}\right|_{V_0,T_0}.$$

The difference between the Euler and Lagrange approaches to deformation description can be explained as follows. Consider an isotropic specimen in the form of a cube of side l_0 in the undeformed state, which undergoes hydrostatic compression. In the deformed state, the side of the cube is l, with $l = \xi l_0$. The Lagrange and Euler measures expressed in terms of ξ can be repre-

sented as follows:

$$\varepsilon_L = \frac{1}{2}(\xi^2 - 1), \tag{20}$$

$$\varepsilon_E = \frac{1}{2}(1 - \xi^{-2}), \tag{21}$$

where

$$\xi = l/l_0 = (V/V_0)^{\frac{1}{3}}.$$

Figure 1 shows graphs for these. At small deformations ($\xi \approx 1$), the two measures are virtually the same, while the Euler measure is unsatisfactory for large degrees of stretching (i.e., it is necessary to retain a large number of terms in the expansion of (2) for the free energy), whereas the Lagrange measure is unsuitable for describing finite compression deformations.

Both approaches are used in constructing equations of state [14, 15, 17, 18, 20], but with a given number of terms in (2) the Euler approach gives better agreement with measurements on the compressibility (see below). This approach has been widely used in describing isothermal P-V compression curves. The equation of state (19) is called the Birch-Murnaghan equation and is usually written as

$$P = \frac{3}{2}K_{0T}\left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}}\right]\left\{1 - \frac{3}{4}(K'_{0T}-4)\left[\left(\frac{V}{V_0}\right)^{-\frac{2}{3}}-1\right]\right\}. \tag{22}$$

In a series of papers, Ullman and Pan'kov [14, 15] considered the definition of a deformation measure that is parametrically dependent on the bulk modulus and its derivatives with respect to pressure in the reference state and which enables us to reduce the number of terms in (2) without loss of accuracy. Several deformation measures were proposed depending on which derivatives of the bulk modulus were used, of which the simplest is

$$\varepsilon_{U-P} = \frac{1}{u}\left[\left(\frac{V}{V_0}\right)^{u-1} - 1\right], \tag{23}$$

where $u = (2 - K'_{0T})/3$, $K'_{0T} > 2$. The corresponding three-parameter equation of state takes the form

$$P = -\frac{K_{0T}}{u}\left[\left(\frac{V}{V_0}\right)^{2u-1} - \left(\frac{V}{V_0}\right)^{u-1}\right]. \tag{24}$$

It was shown [14, 15] for numerous compounds that the theoretical isotherms of (24) for $T = 298$ K agree very well with experimental data down to $V/V_0 = 0.6$.

Some simple hypotheses on the pressure dependence of the bulk modulus enable us to obtain equations of state by direct integration. For example, Murnaghan's equation [21]

$$P = \frac{K_{0T}}{K'_{0T}}\left[\left(\frac{V}{V_0}\right)^{-K'_{0T}} - 1\right] \tag{25}$$

was derived on the assumption of linear pressure dependence of the bulk modulus, i.e.,

$$K_T(P) = K_{0T} + K'_{0T}P.$$

Tait's equation is often used to describe the P-V-T properties of dense gases at elevated pressures, but virtually no study has been made of its applicability to solids over wide temperature and pressure ranges. In the terms used here,
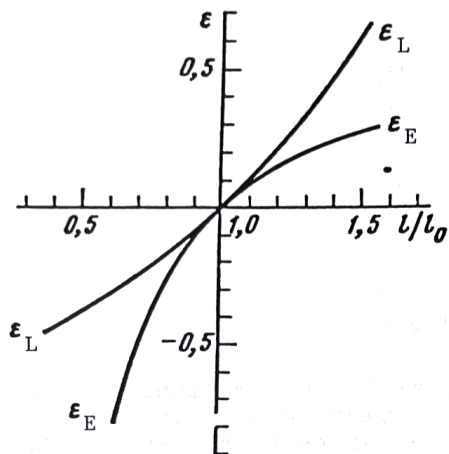
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Fig. 1. Dependence of the Euler
and Lagrange deformation measures
on the change in linear size of
an isotropic solid.

Tait's equation may be put [20] in the form

$$P = \frac{K_{0T}}{K'_{0T}+1} \left[e^{(K'_{0T}+1)\left(1-\frac{V}{V_0}\right)} - 1 \right].$$ (26)

Numerous examples of empirical equations of state are discussed in reviews [14, 20].

To construct an isothermal equation of state by the above methods it is necessary to specify at least three parameters: the molar volume, the isothermal bulk modulus, and the derivative of this with respect to pressure. All these methods define the P-V relationship at a certain fixed temperature (usually 298 K) and do not allow us to pass directly from one isotherm to another. To derive the high-temperature isotherms requires additional information on the temperature dependence of the parameters in the equation of state. As the derivatives of the bulk modulus with respect to pressure are at present known with low accuracy, we usually neglect the temperature dependence of these.

Let us consider in more detail one of the methods of calculating the temperature dependence of K_T at atmospheric pressure [26]. This is based on a fact derived from ultrasonic experiments, namely that

$$\gamma = \frac{\alpha K_S V}{c_p} \bigg|_{P=0},$$ (27)

$$\delta_S = -\frac{1}{\alpha K_S} \frac{\partial K_S}{\partial T} \bigg|_{P=0}$$ (28)

are virtually independent of temperature. Here $\alpha = 1/V(\partial V/\partial T)_P$ is the thermal-expansion coefficient and $K_S = -V(\partial P/\partial V)_S$ is the adiabatic bulk modulus, with c_p the molar specific heat at constant pressure, γ the Grüneisen parameter, and δ_S the Anderson-Grüneisen parameter.

The following applies for the temperature dependence of the bulk modulus at $P=0$:

$$K_S(T) = K_S(298) + \int_{298}^{T} \frac{\partial K_S}{\partial T} \, dT.$$ (29)

From (27) and (28) we have

$$\left(\frac{\partial K_S}{\partial T}\right)_P = -\frac{\gamma \delta_S c_p(T)}{V(T)}.$$ (30)

Of the four quantities on the right in (30), only c_p and V are dependent on

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temperature. Then from (29) and (30) we get

$$K_S(T) = K_S(298) - \gamma\delta_S \int_{298}^{T} \frac{c_p(T)}{V(T)} dT. \tag{31}$$

As αT is small, the integral in (31) can be transformed to the following without substantial loss of accuracy:

$$\int_{298}^{T} \frac{c_p}{V} dT = \frac{1}{V(298)} \int_{298}^{T} \frac{c_p}{1+\alpha T} dT \approx \frac{1}{V(298)} \int_{298}^{T} c_p(1-\alpha T) dT. \tag{32}$$

Using the definition of enthalpy $dH = c_p dT$ and with the aid of (32), we can transform (31) to

$$K_S(T) = K_S(298) - \frac{\gamma\delta_S}{V(298)} \left[(H_T - H_{298}) - \int_{298}^{T} c_p \alpha T\, dT \right]. \tag{33}$$

The integral on the right in (33) may be determined numerically, but in most practical cases it can be put equal to $\alpha T(H_T - H_{298})/2$. Then finally we have

$$K_S(T) = K_S(298) - \frac{\gamma\delta_S}{V(298)} (H_T - H_{298}) \left(1 - \frac{\alpha T}{2} \right). \tag{34}$$

The values of the isothermal bulk modulus and volume can now be determined by means of thermodynamic relations:

$$K_T(T) = K_S(T)/(1 + \alpha\gamma T), \tag{35}$$

$$V(T) = V(298) \exp\left(\int_{298}^{T} \alpha\, dT \right). \tag{36}$$

Thus, this method of calculating $K_T(T)$ and $V(T)$ at 1 atm and high temperatures enables us to incorporate the temperature dependence of the parameters in semiempirical equations of state for solids in a simple fashion, but it requires information on the derivative of the bulk modulus K_S with respect to temperature, which at present is known only for a restricted number of compounds.

CONSTRUCTION OF AN EQUATION OF STATE FOR A SOLID FROM THE
QUASIHARMONIC APPROXIMATION

A second group of methods is based on concepts from statistical physics, according to which the free energy of a solid $F(V, T)$ can be represented as the sum of two terms: a potential one $E_p(V)$ dependent only on the volume and a thermal one $F_T(V, T)$, which characterizes the zero-point and thermally excited vibrations of the lattice atoms [27, 28], with anharmonic effects neglected:

$$F(V, T) = E_p(V) + F_T(V, T) = E_p(V) + E_T(V, T) - TS(V, T), \tag{37}'$$

where $S(V, T)$ is entropy. The form of $E_p(V)$ is established from a particular model for the atomic interaction. The thermal component $F_T(V, T)$ is generally described by means of the quasiharmonic approximation [1, 18, 27, 28], in which the solid is considered as a set of independent harmonic oscillators. Then the free energy of (37) can be put as

$$F(V, T) = E_p(V) + \frac{1}{2} \sum_\alpha \hbar\omega_\alpha + kT \sum_\alpha \ln(1 - e^{-\frac{\hbar\omega_\alpha}{kT}}), \tag{38}$$

hwere $\hbar$ and k are Planck's and Boltzmann's constants, while $\omega_\alpha(V)$ are the oscillator frequencies, which are dependent on volume. In the quasiharmonic approximation it is assumed that deformation alters the average positions of the atoms, which affects the frequencies ω_α, while the oscillations themselves remain essentially harmonic. The ratio of the relative frequency change $\Delta\omega_\alpha/\omega_\alpha$ to the relative volume change $\Delta V/V$ is called the partial Grüneisen parameter γ_α:

$$\gamma_\alpha = \frac{d\ln\omega_\alpha}{d\ln V}. \tag{39}$$

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Differentiation of (38) with respect to volume gives an equation of state of the form

$$P(V,T) = P_p(V) + \frac{1}{V}\sum_\alpha \gamma_\alpha E_\alpha,$$

(40)

where $P_p(V) = -\dfrac{dE_p}{dV}$ is the potential pressure and

$$E_\alpha = \frac{\hbar\omega_\alpha}{2} + \frac{\hbar\omega_\alpha}{\exp\left(\dfrac{\hbar\omega_\alpha}{kT}\right) - 1}.$$

(41)

is the energy of oscillator α [27, 28], $E_\alpha = F_\alpha - T(\partial F_\alpha/\partial T)_V$. The assumption that all the partial γ_α are equal leads to the Mie-Grüneisen equation [1, 17, 18]:

$$P(V\ T) = P_p(V) + \frac{\gamma}{V}E_T(V,T),$$

(42)

where

$$E_T(V,T) = \sum_\alpha E_\alpha$$

(43)

is the thermal component of the internal energy.

In the limiting case of high temperatures $(\hbar\omega_\alpha < kT)$, from (41) we have

$$E_\alpha \approx kT,$$

(44)

i.e., the energy of each of the harmonic oscillators is linear with respect to temperature and independent of volume. This will also apply to the thermal component of the internal energy of (43). Then on differentiating the free energy of (37) with respect to volume, the term $(\partial E_T/\partial V)_T$ can be neglected:

$$P(V,T) = -\left(\frac{\partial F}{\partial V}\right)_T = P_p(V) + T\left(\frac{\partial S}{\partial V}\right)_T.$$

(45)

As

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T,$$

(46)

we arrive at an equation of state in the Hildebrandt form [29]:

$$P(V,T) = P_p(V) + \alpha K_T T.$$

(47)

Anderson's review [29] deals with the basis for using Hildebrandt's approximation in constructing equations of states for solids. According to (29), at temperatures close to the Debye value and above, the product αK_T is approximately constant and is independent of pressure and temperature.

In the practical use of (42) and (47), there can be various realizations dependent on the form used for the potential $E_p(V)$ and the method of calculating the parameters. The potential method is widely used within the framework of the Mie-Grüneisen approximation. See [1] for details of the physical basis for this and the use of it in constructing equations of state for solid phases from experimental compression curves.

The potential components of the internal energy and pressure are described by the following expressions* in the potential method [1]:

$$E_p(x) = \frac{3A}{b\rho_0}e^{b(1-x^{\frac{1}{3}})} - \frac{3K}{\rho_0}x^{-\frac{1}{3}},$$

(48)

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*Other forms of the potentials are discussed in [1, 14, 20, 30].

$$P_p(x) = Ax^{-\frac{2}{3}} e^{b(1-x^{\frac{1}{3}})} - Kx^{-\frac{4}{3}}, \tag{49}$$

where $x = \rho_0/\rho = V/V_0$ is the dimensionless volume, ρ_0 is the density of the substance under normal conditions ($T = 298$ K, $P = 0$, $x = 1$), ρ is the density under P—T conditions, and A, b, and K are parameters of the potential, which are determined indirectly from experimental compressibility data.

The thermal component of the internal energy is calculated in the Debye approximation [1, 28]:

$$E_T(x, T) = \frac{R}{\mu} \left[\frac{9}{8} \theta + 3TD\left(\frac{\theta}{T}\right) \right], \tag{50}$$

where R is the universal gas constant, μ is the mean molecular mass, $D(\theta/T)$ is the Debye function, and θ is the Debye temperature, which is related to the Grüneisen parameter as follows:

$$\theta(x) = \theta_0 \exp\left(\int_x^1 \frac{\gamma}{x} \, dx \right). \tag{51}$$

A generalized formula is used [9] for the Grüneisen parameter:

$$\gamma(x) = -\frac{x}{2} \frac{d^2(P_p x^m)/dx^2}{d(P_p x^m)/dx} + \frac{3m-4}{6}, \tag{52}$$

where m is the parameter whose value may be found from the condition that the γ of (52) under normal conditions coincides with the thermodynamic value from (27) [5].

In the potential method devised by Zharkov and Kalinin [1, 12, 13], the parameters A, b and K are determined by means of an optimization procedure from the condition for best fit to the experimental compression curves: the isotherm at 298 K, the shock adiabatics, and curves relating the seismic parameter to volume. However, as we have pointed out above, it is best to operate at the level of elastic constants at normal pressure in thermodynamic calculations and in the analysis and matching of experimental compressibility data.

A modified form of the potential method has been devised [5, 11] for use in physicochemical and geochemical applications, in which the parameters in the equation of state are derived from measurements on the elastic and caloric constants K_S, K_S', c_p, α, ρ, and θ at normal pressure. Details of the procedure for calculating the parameters can be found in [5].

The Mie-Grüneisen equation of (42) realized in the potential method is thermal, which is a difference from the equations of state derived by methods from the theory of elasticity, i.e., it contains thermal terms in explicit form and enables us to calculate the entire P-V-T surface for the solid.

CONSTRUCTION OF AN EQUATION OF STATE FOR A SOLID BY METHODS FROM THE THEORY OF ELASTICITY IN THE QUASIHARMONIC APPROXIMATION

A theory has been devised [17, 18] for the thermal equation of state of a solid that combines the principles of the phenomenological and atomistic approaches. A distinctive feature of this approach is that the temperature dependence of the coefficients in (2) is found by comparing (5)-(7) with analogous formulas in the quasiharmonic approximation.

We see from (5) that the first coefficient in the free-energy expansion is equal to the pressure in the reference state V_0, T_0, apart from a constant factor. The change when the temperature increases from T_0 to T will be determined by the difference of the pressures in the states V_0, T and T_0, T_0, which according to (42) is

$$P(V_0, T) - P(V_0, T_0) = \frac{\gamma_0}{V_0} [E_T(V_0, T) - E_T(V_0, T_0)]. \tag{53}$$

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Then (5) becomes

$$\left.\frac{\partial F}{\partial \varepsilon}\right|_{V_0, T} = \left.\frac{\partial F}{\partial \varepsilon}\right|_{V_0, T_0} - \frac{\gamma_0}{V_0} [E_T(V_0, T) - E_T(V_0, T_0)] \frac{\partial V}{\partial \varepsilon}.$$

(54)

The temperature dependence of the second coefficient in (2) can be written as follows on the basis of (6):

$$\left.\frac{\partial^2 F}{\partial \varepsilon^2}\right|_{V_0, T} = \left.\frac{\partial^2 F}{\partial \varepsilon^2}\right|_{V_0, T_0} + \frac{1}{V_0} [K_T(V_0, T) - K_T(V_0, T_0)] \times$$
$$\times \left(\frac{\partial V}{\partial \varepsilon}\right)^2 - [P(V_0, T) - P(V_0, T_0)] \frac{\partial^2 V}{\partial \varepsilon^2}.$$

(54a)

The temperature dependence of the isothermal bulk modulus K_T can be determined by substituting (42) into (4). Then

$$K_T = K_p + \left(1 + \gamma - \frac{\partial \ln \gamma}{\partial \ln V}\right) \frac{\gamma}{V} E_T - \frac{\gamma^2}{V} T c_v,$$

(55)

where $K_p(V) = -V \frac{dP_p}{dV}$ is the potential component of the bulk modulus and $c_v(V, T)$ is the specific heat at constant volume.

To calculate E_T and c_v, the Debye approximation is usually used. The quantity $\partial \ln \gamma / \partial \ln V$ can be calculated by means of a standard thermodynamic relation [29]:

$$\frac{\partial \ln \gamma}{\partial \ln V} = \delta_S + \gamma - K_S' + 1,$$

(56)

where δ_S is the Anderson-Grüneisen parameter, for which see (28), and K_S' = $(\partial K_S / \partial P)_T$. The coefficients in (2) beginning with the third are related to the bulk modulus with respect to pressure. There is at present no experimental information on the temperature dependence of such quantities, and also the quasiharmonic approximation is based on expanding the potential energy only up to the second order, and therefore the contribution from the quasiharmonic terms to the higher-order coefficients may be neglected [18].

Therefore, the temperature dependence of the free-energy expansion of (2) and in equations of state based on it such as (14) and (19) may be incorporated in the quasiharmonic approximation by means of the first two coefficients, which are defined by (5) with (54) and (6) with (54a) respectively. In each particular case, these sets of equations provide the corresponding working formulas in accordance with the deformation measure $\varepsilon(V/V_0)$ used. For example, normal conditions may be taken as the reference state (T_0 = 298 K, P_0 = 0), in which case we obtain the following third-order thermal equations of state in the Lagrange and Euler approaches.

Lagrange approach:

$$\varepsilon_L = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right],$$

$$P(\varepsilon_L, T) = -\frac{(1 + 2\varepsilon_L)^{\frac{1}{2}}}{3V_0}(b_0 + b_1\varepsilon_L + b_2\varepsilon_L^2),$$

$$b_0(T) = -3\gamma_0 [E_T(V_0, T) - E_T(V_0, T_0)],$$

$$b_1(T) = 9V_0K_{0T} + \left(3\frac{\partial \ln \gamma}{\partial \ln V} - 3\gamma_0 - 2\right)b_0(T) - 9\gamma_0^2 [Tc_V(V_0, T) - T_0c_V(V_0, T_0)],$$

$$b_2 = -\frac{27}{2}V_0K_{0T}K_{0T}'.$$

(57)

Euler approach:

$$\varepsilon_E = \frac{1}{2}\left[1 - \left(\frac{V}{V_0}\right)^{-\frac{2}{3}}\right],$$

$$P(\varepsilon_E, T) = -\frac{(1-2\varepsilon_E)^{\frac{5}{2}}}{3V_0}(c_0 + c_1\varepsilon_E + c_2\varepsilon_E^2),$$

$$c_0(T) = -3\gamma_0[E_T(V_0, T) - E_T(V_0, T_0)],$$

$$c_1(T) = 9V_0K_{0T} + \left(3\frac{\partial \ln \gamma}{\partial \ln V} - 3\gamma_0 + 2\right)c_0(T) - 9\gamma_0^2[Tc_V(V_0, T) - T_0c_V(V_0, T_0)],$$

$$c_2 = -\frac{27}{2} V_0K_{0T}(K_{0T}' - 4). \tag{58}$$

COMPARISON OF THE THERMAL EQUATIONS OF STATE AND THE INTEGRALS $\int_0^P VdP$

FOR PERICLASE, FORSTERITE AND PYROPE

Calculations of P-T curves for chemical and phase equilibria require information on $\int_0^P VdP$; but inadequate attention has been given to the reliability of these quantities up to now in thermodynamic calculations. It is therefore necessary to examine the sensitivity of the isothermal P-V curves and $\int_0^P VdP$ to the method of constructing the thermal equation of state, and it is also necessary to estimate the random errors.

To compare the results based on equations of state obtained by different methods let us consider three compounds differing in composition and structure: periclase MgO, forsterite α-Mg_2SiO_4, and pyrope $Mg_3Al_2Si_3O_{12}$. Surveys have been made of the experimental data on the elastic constants, specific heats, and thermal expansion of these substances [4, 5, 11, 31]. Table 1 gives the initial experimental data on the elastic and caloric characteristics of the compounds at 1 atm and 298 K as required to construct the thermal equations of state. The values of K_S, K_S', θ, α, c_p, ρ, and γ for normal conditions and the potential parameters for these phases have been calculated previously [5, 11, 31]. The values of K_T have been derived from (35) using the known K_S, α, and γ. The δ_S were calculated via (28) from the acoustic data.

Universal FORTRAN programs were written to construct the equations of state.

Isotherms at 298 and 2000 K. The accuracy of the semiempirical equations derived by elastic-theory methods is dependent on the number of terms used in the series of (2). In the construction, we use mainly expansions up to the third order (i.e., up to terms containing $K_T' = \partial K_T/\partial P$), since the derivatives of higher orders cannot at present be determined with acceptable accuracy. Then the equations of state contain the three parameters V_0, K_{0T}, and $K_{0T'}$.

Figure 2 shows the behavior of the three-parameter equations of state (14), (22), (24), and (25) for periclase at 298 K, together with the experimental data on static compression [32-34] and the theoretical isotherm calculated by the potential method from (42) and (49)-(52). The curves calculated from the Birch-Murnaghan (22), Ullman-Pan'kov (24), and Murnaghan (25) equations, and by the potential method agree with the experiment within the errors of the measurements (6% in pressure [32]). The isotherms derived from (22) with (24) and from (42) with (49)-(52) at 298 K are practically indistinguishable up to a pressure of 1 Mbar. On the other hand, the third-order Lagrange isotherm of (14) systematically underestimates the pressure at P above 200 kbar. The errors in the experimental data and the calculations make it difficult to give

Table 1

Thermodynamic Constants and Parameters in the Equations of State for Periclase, Forsterite, and Pyrope under Normal Conditions

Constants and parameters	MgO	α-Mg$_2$SiO$_4$	Mg$_3$Al$_2$Si$_3$O$_{12}$
ρ, g/cm^3	3,583 (0,001)	3,213 (0,001)	3,559 (0,001)
K_S, kbar	1630 (10)	1288 (10)	1770 (10)
K_S'	4,5 (0,25)	5,1 (0,2)	4,5 (0,25)
K_T, kbar	1607	1276	1758
K_T'	4,5	5,1	4,5
θ, K	936 (5)	763 (5)	788 (5)
$\alpha \cdot 10^6$, K^{-1}	31,2 (0,5)	26,0 (0,5)	19,0 (0,5)
c_p, cal/mol·deg	9,03 (0,03)	28,18 (0,07)	77,75 (0,20)
δ_S	3,9	4,2	5,9
γ	1,52 (0,03)	1,24 (0,03)	1,17 (0,03)
A, kbar	714,187 (92,3)	446,801 (31,3)	776,753 (83,1)
b	8,7613 (0,873)	10.5202 (0,593)	8,7827 (0,724)
K, kbar	743,097 (92,3)	466,056 (31,3)	797,059 (83,1)

Table 2

Temperature Dependence of the Molar Volumes and Bulk Moduli at Atmospheric Pressure

Compound	T, K	$\alpha \cdot 10^6$, K^{-1}	V_0, cm^3/mol	K_S, kbar	K_T, kbar
MgO	298	31,2	11,25	1630	1607
	1000	45	11,55	1495	1395
	2000	54	12,15	1289	1100
α-Mg$_2$SiO$_4$	298	26	43,79	1288	1276
	1000	38	44,76	1160	1110
	2000	47	46,59	950	850
Mg$_3$Al$_2$Si$_3$O$_{12}$	298	19	113,29	1770	1758
	1000	29	115,20	1576	1524
	2000	33	118,40	1290	1200

preference to any of these equations, but we note that the third-order Lagrange equation (14) is evidently not applicable to describing the compressibility above 200 kbar.

The temperature dependence in the three-parameter equations of state (14), (22), (24), and (25) may be incorporated directly by means of the parameters $V_0(T)$, $K_{0T}(T)$, and $K_{0T}'(T)$ without involving quantum-statistical concepts. According to (35), the derivative of the isothermal bulk modulus with respect to pressure K_T' for periclase at $P = 0$ is virtually independent of temperature, so it can be taken as constant in the calculations. Table gives the high-temperature values of $K_{0S}(T), K_{0T}(T)$, and $V_0(T)$ for periclase, forsterite, and pyrope calculated from (34)-(36). The temperature dependence of the thermal-expansion coefficients was taken from [34, 37]. There are no data for α for pyrope at $T > 1073$ K, so the value of α at 2000 K is to be considered as an estimate.
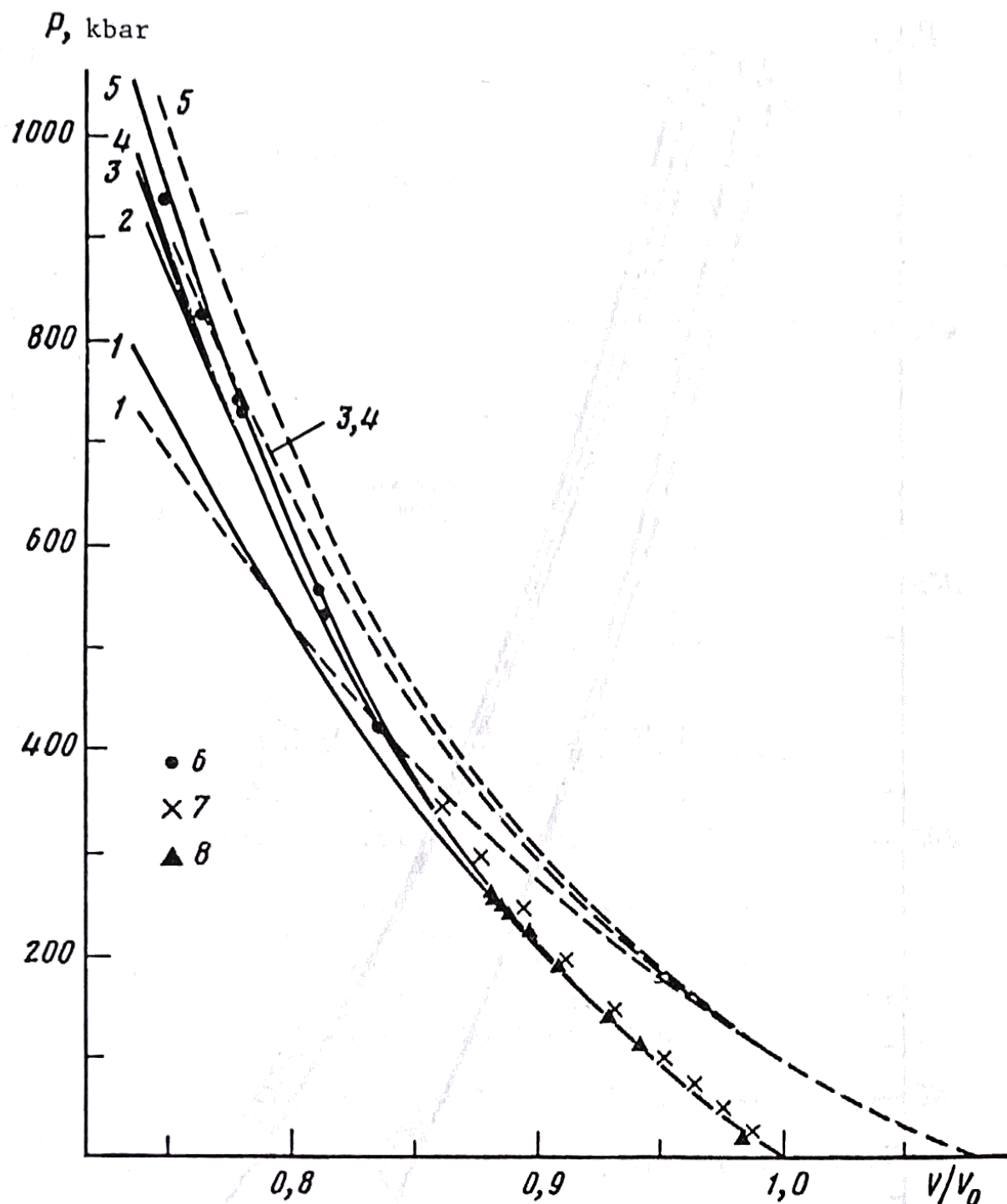
Fig. 2. Isotherms for periclase at 298 K (solid lines) and 2000 K (broken lines). Methods: 1) third-order Lagrange (14), 2) potential (42) and (49)-(52), 3) third-order Euler (19), 4) Ullman-Pan'kov (24), 5) Murnaghan (25), 6) experiment [32], 7) experiment [33], 8) experiment [34].

The isotherms of (14), (22), (24), and (25) for periclase calculated for 2000 K from the data of Table 2 are shown by broken lines in Fig. 2. The curves agree well with one another up to 200 kbar, but at higher pressures the 2000 K isotherm given by the Lagrange approach of (14) deviates substantially from the other curves towards lower pressures, and at $P \approx 500$ kbar it intersects the 298 K isotherm, which is physically meaningless. Tait's equation (26) describes the 298 K isotherm very well: the $P-V$ points virtually coincide with those calculated by the potential method. On the other hand, the compression curve at 2000 K deviates substantially from that constructed by the potential method, and at $P \approx 600$ kbar it intersects the 298 K isotherm. At pressures of ~1 Mbar, this occurs also for the Birch-Murnaghan equation of (22). The reason for this is that the volume of the body increases with temperature at $P = 0$, and the isothermal bulk modulus K_T decreases. Then the point on the isotherm $V(P = 0)$ is displaced towards larger volumes, and the inclination of the isotherm to the abscissa (which by definition is proportional to K_T) decreases. If the value of K_T' is fixed, the isotherms intersect at a certain pressure. There are no experimental data on static compression at high temperatures, so it is not possible to perform a rigorous check on the adequacy of the calculated isotherms, and the only criterion here is the correspondence between the results from different methods of constructing the equations of state.

Figure 3 gives 298 and 2000 K isotherms for periclase calculated in the quasiharmonic approximation by the potential method of (42) and (49)-(52) and by Davies's method of (57) and (58).
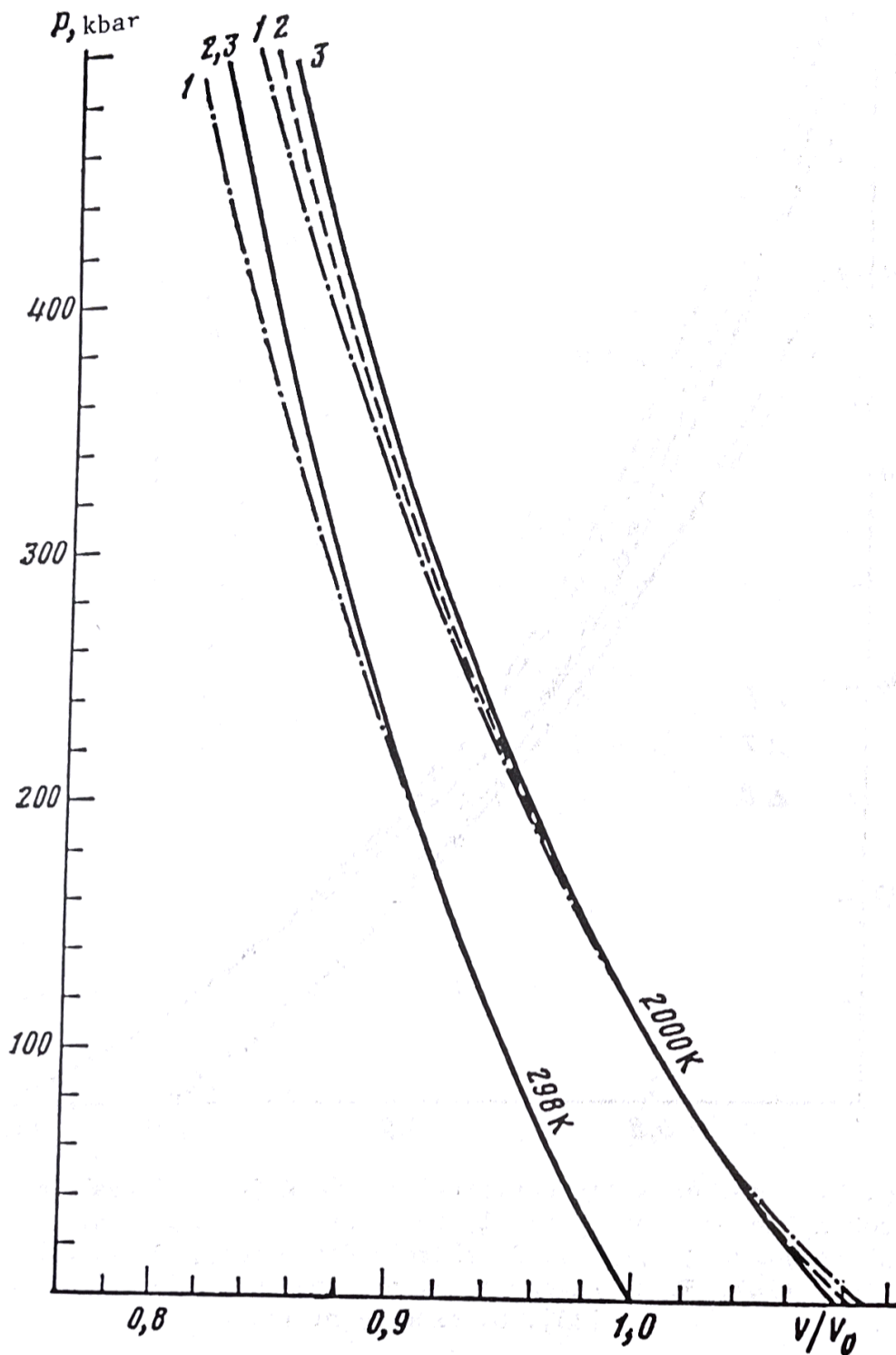
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Fig. 3. 298 and 2000 K isotherms for periclase calculated in the quasiharmonic approximation. Methods: 1) third-order Lagrange (57), 2) third-order Euler (58), 3) potential (42) and (49)-(52).

On the whole, the various methods for periclase give results in good agreement. If we rule out the third-order Lagrange equation, the maximum pressure discrepancy at 298 K for pressures of the order of 1 Mbar is ~70 kbar or 7%. Approximately the same error applies for current methods of static and shock compression at these parameters.

The various methods give fairly similar results for the temperature dependence of the equations of state at low degrees of compression. For example, the discrepancy between the curves (Fig. 4) at $V/V_{298} = 0.9$ is not more than 10% of the increment in the thermal pressure. However, on the whole the agreement between the different methods for the high-temperature isotherms is substantially worse than that for 298 K. The same applies for forsterite and pyrope, whose isotherms are given in Figs. 5 and 6.

Values of $\int_0^P V dP$ at 298 and 2000 K. The values of $\int_0^P V dP$ are calculated by integration by parts:
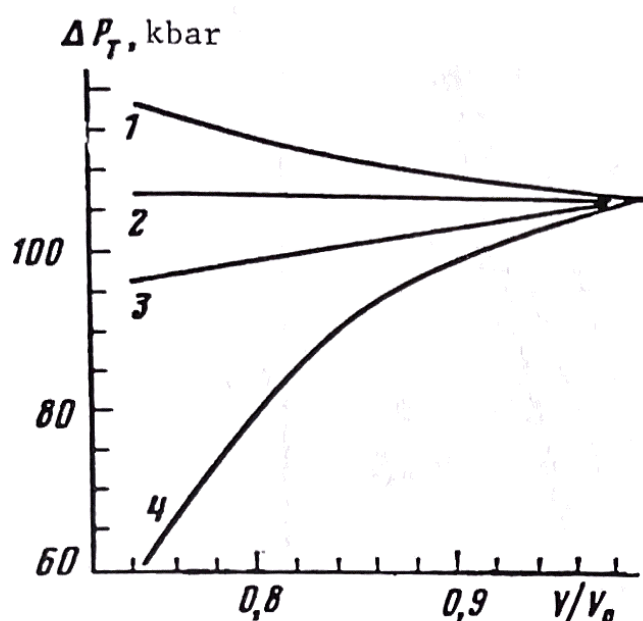
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Fig. 4. Dependence on degree of compression for the increment in the thermal pressure $\Delta P_T = P(V, 2000) - P(V, 298)$ for periclase. Methods: 1) potential (42) and (49)-(52), 2) Hildebrandt (47), 3) third-order Lagrange (57), 4) third-order Euler (58).

$$\int_0^P V\,dP = [VP(V,T) + F(V,T)]\Big|_{V(0,T)}^{V(P,T)}, \qquad (59)$$

where $F(V, T)$ is the Helmholtz free energy.

$F(V, T)$ is known in analytic form for all these methods of constructing the thermal equation of state, namely (2) and (37), while the corresponding working formulas for Murnaghan's and Tait's equations may be obtained by analytic integration of (25) and (26). The lower limit of integration $V(0, T)$ is found by numerical solution of equation $P(V, T) = 0$. Then with a fixed step in V calculate the pressure and $\int_0^P V\,dP$. Table 3 gives values of the integrals obtained by various methods as interpolated with respect to pressure. The values of $\int_0^P V\,dP$ calculated from the various equations of state are seen to agree well. For example, for periclase at 298 K the discrepancy between the values of $\int_0^P V\,dP$ even at 400 kbar lies only in the second decimal place and is on the order of 0.01%. The values of $\int_0^P V\,dP$ calculated from the equations of state with Lagrange deformation measure are low, which is explained by the behavior of the corresponding compression curves (Fig. 2). The same applies for forsterite and pyrope. The quasiharmonic approximation of (57) leads to a more reasonable description of the thermal corrections than does (14) with the temperature dependence for the bulk modulus of (31)-(34) and the volume variation of (36). The discrepancies between the values of the integrals calculated from all the equations of state at 298 K and 400 kbar are only 0.2% for forsterite and pyrope.

The empirical equations of Murnaghan (25) and Tait (26) agree well with other methods in the calculation of $\int_0^P V\,dP$ at 298 K, but they result in low values at high temperatures and at pressures exceeding $\sim K_T/4$.

On the whole, the discrepancies in the values of the integrals for the high-temperature isotherms are somewhat higher than those at 298 K, but even in the megabar range they do not exceed the errors of current thermodynamic data at 1 atm. For example, the maximum discrepancies in the values of the integrals at 400 kbar and 2000 K (Table 3) are not more than 1% for periclase, 1.3% for forsterite, and 2% for pyrope. This occurs because $\int_0^P V\,dP$ is an integral characteristic of the equation of state which is equal to the area bounded by the isotherm and the pressure axis; minor perturbations in the slope of the isotherms have virtually no effect on the area.
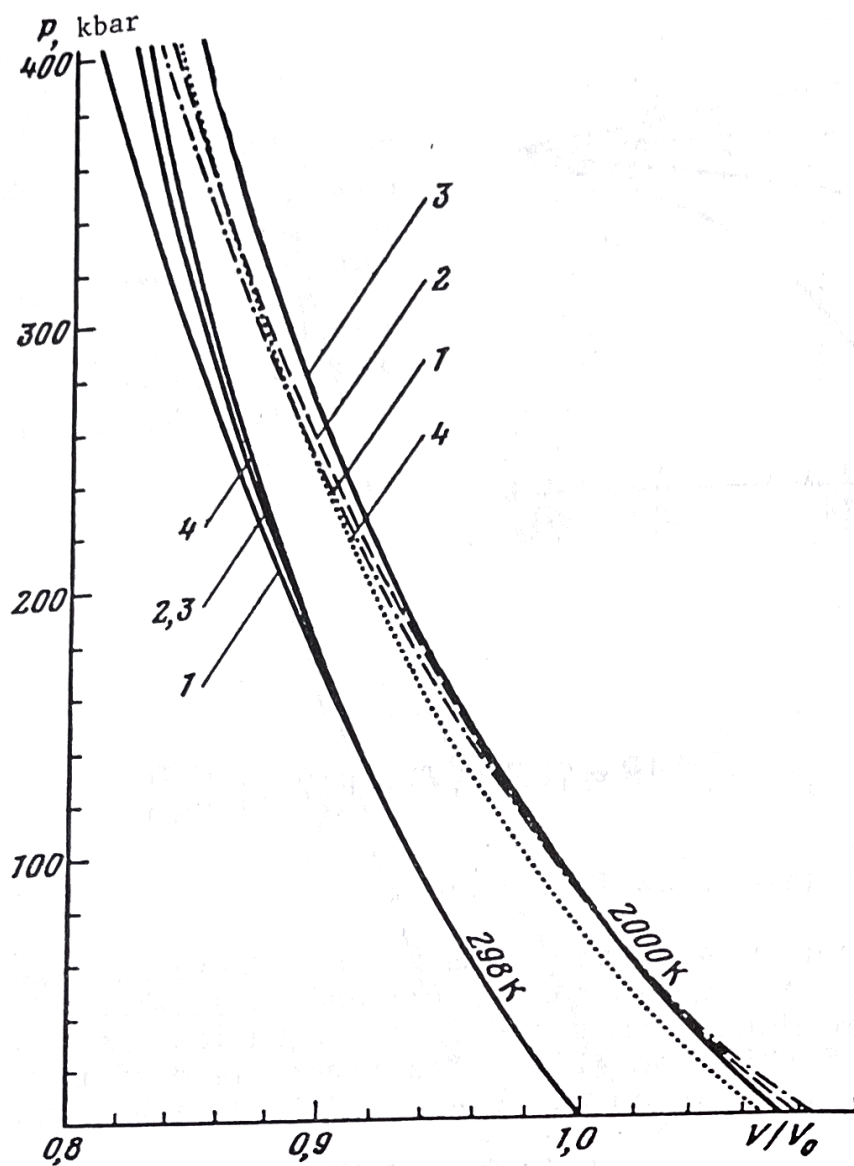
Fig. 5. 298 and 2000 K isotherms for forsterite.
Methods: 1) third-order Lagrange (57), 2) third-
order Euler (58), 3) potential (42) and (49)-(52),
4) Murnaghan (25).

In fact, we can estimate the sensitivity of $\int_0^P V\,dP$ to variations in the $V(P)$ curve for given T.

Let us represent the equation of state in the form

$$\tilde{V}(P, T) = V(P, T) + \delta V(P, T), \tag{60}$$

where $V(P, T)$ is the true value of the molar volume and $\delta V(P, T)$ is the deviation from the true value. Then the error in the integral will be

$$\delta \int V\,dP = \int \tilde{V}\,dP - \int V\,dP = \int \delta V\,dP. \tag{61}$$

From known values of $\delta V(P)$ we estimate $\delta \int V\,dP$ on the basis that $\delta V(0) = 0$. Without loss of accuracy we can assume that the uncertainty in the values of $V(P)$ is characterized by the relationship

$$\delta V(P) = \eta P. \tag{62}$$

We substitute (62) into (61) to get

$$\delta \int_0^P V\,dP = \frac{\eta P^2}{2}. \tag{63}$$

For periclase at 1 Mbar and 298 K we have $\delta V/V_0 \approx 1\%$, and then $\eta = V_0 \cdot 10^{-5}$ and $\delta \int_0^P V\,dP \approx 1$ kcal/mol, which corresponds to a relative error of $<1\%$. Note that
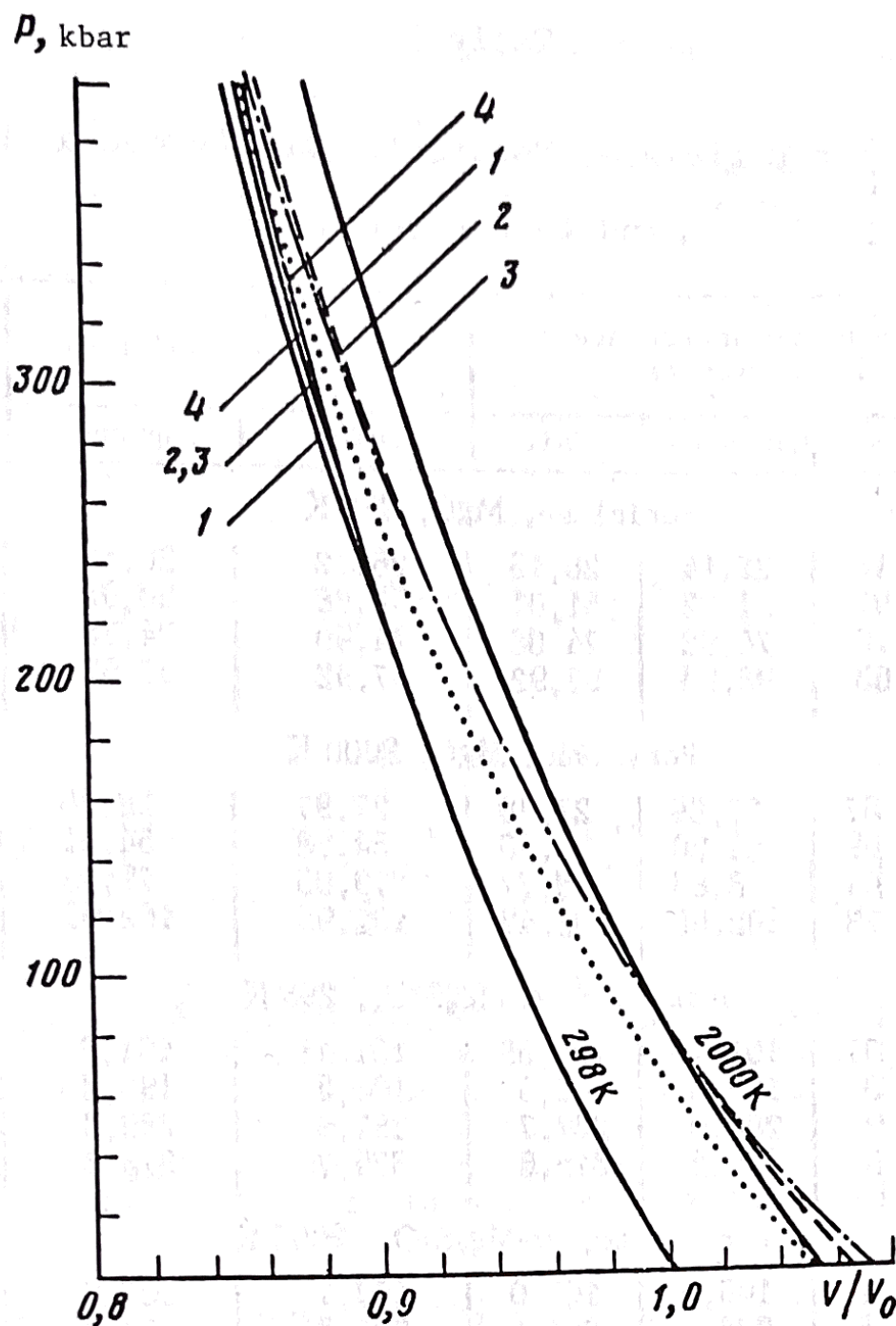
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Fig. 6. 298 and 2000 K isotherms for pyrope.
Methods: 1) third-order Lagrange (57), 2) third-
order Euler (58), 3) potential (42) and (49)-(52),
4) Murnaghan (25).

the function $P(V)$ is recovered with more uncertainty than is $V(P)$. For example,

$$\frac{\delta P(V)}{P} \sim \frac{K_T}{P} \cdot \frac{\delta V}{V} \approx 10\%.$$

Therefore, the calculations show that $\int_0^P V\,dP$ is determined with high accuracy, which substantially exceeds the accuracy of the $P-V-T$ data, and within the errors of the calculations it is independent of the model and the method of constructing the equation of state. This results in the important conclusion that one obtains reliable results from thermodynamic calculations on chemical and phase transformations for the P and T conditions of the mantle and for the planets of the terrestrial group.

ESTIMATING THE ERRORS OF THE THERMAL EQUATION OF STATE DERIVED FROM THE POTENTIAL METHOD

We examined the sensitivity of the equation of state and of the integrals to errors in the initial experimental data by reference to the modified potential method [5]. The standard formula from the theory of error propagation [38] is used:

$$\sigma_y^2 = \sum_{i,j} \left(\frac{\partial y}{\partial a_i}\right)\left(\frac{\partial y}{\partial a_j}\right) \sigma_{ij}^2 \qquad (64)$$

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Table 3

Values of $\int_0^P VdP$ for Periclase, Forsterite and Pyrope at High Pressure and Temperatures

P, kbar	From temperature dependence of $V_0(T)$ and $K_{0T}(T)$				Davies's method [18]		Potential method [5]
	Euler	Lagrange	Murnaghan	Tait	Euler	Lagrange	
Periclase, MgO, 298 K							
100	26,13	26,13	26,14	26,13	26,12	26,12	26,13 (0,1)
200	51,01	50,97	51,02	51,01	50,98	50,95	51,00 (0,1)
300	74,89	74,76	74,92	74,88	74,90	74,75	74,87 (0,3)
400	97,95	97,63	98,03	97,92	97,92	97,62	97,93 (0,6)
Periclase, MgO, 2000 K							
100	27,88	27,87	27,88	27,90	27,97	28,00	27,94 (0,2)
200	53,97	53,89	54,20	54,00	54,18	54,21	54,18 (0,2)
300	78,75	78,44	78,83	78,77	79,05	79,08	79,16 (0,3)
400	102,48	102,78	102,65	102,47	102,95	102,91	103,13 (0,6)
Forsterite, α-Mg$_2$SiO$_4$, 298 K							
100	101,09	101,07	101,10	101,09	101,11	101,07	101,05 (0,1)
200	196,5	196,3	196,6	196,5	196,5	196,3	196,4 (0,1)
300	287,8	286,9	288,0	287,7	287,6	286,8	287,6 (0,3)
400	375,6	373,5	376,2	375,6	375,7	373,3	375,4 (0,5)
Forsterite, α-Mg$_2$SiO$_4$, 2000 K							
100	106,5	106,4	106,5	106,0	107,7	107,8	107,3 (0,3)
200	205,2	204,6	205,4	204,1	207,3	207,4	207,3 (0,5)
300	298,6	296,6	299,1	296,7	301,1	301,4	302,2 (0,6)
400	387,9	383,6	389,0	385,2	391,5	390,9	393,0 (0,8)
Pyrope, Mg$_3$Al$_2$Si$_3$O$_{12}$, 298 K							
100	263,77	263,74	263,77	263,77	263,62	263,59	263,63 (0,1)
200	515,7	515,4	515,8	515,7	515,4	515,1	515,4 (0,1)
300	758,2	757,1	758,4	758,1	757,8	756,7	757,6 (0,2)
400	992,7	990,0	993,4	992,5	992,2	989,5	991,9 (0,4)
Pyrope, Mg$_3$Al$_2$Si$_3$O$_{12}$, 2000 K							
100	273,7	273,7	273,7	272,7	277,2	277,5	276,1 (0,1)
200	531,0	530,3	531,2	528,9	537,5	537,8	537,8 (0,2)
300	775,9	773,4	776,5	772,7	785,1	785,5	788,4 (0,3)
400	1010,9	1005,1	1012,4	1006,5	1022,7	1022,9	1029,8 (0,6)

where σ_y is the standard deviation of the function y, which is dependent on the random parameters $a_i (i=1, n)$, while σ_{ij}^2 is element i, j of the covariance matrix for the parameters $a_i (i=1, n)$.

In the modified potential method, the initial parameters are K_s, K_s', α, c_p, θ, and ρ under normal conditions. Each of the quantities is evaluated independently in systematizing and selecting the initial data, so the parameters can be taken as independent in the statistical sense. Then for example, for the pressure error formula (64) becomes

$$\sigma_P^2 = \left(\frac{\partial P}{\partial K_S}\right)^2 \sigma_{K_S}^2 + \left(\frac{\partial P}{\partial K_S'}\right)^2 \sigma_{K_S'}^2 + \left(\frac{\partial P}{\partial \alpha}\right)^2 \sigma_\alpha^2 +$$
$$+ \left(\frac{\partial P}{\partial c_p}\right)^2 \sigma_{c_p}^2 + \left(\frac{\partial P}{\partial \theta}\right)^2 \sigma_\theta^2 + \left(\frac{\partial P}{\partial \rho}\right)^2 \sigma_\rho^2. \qquad (65)$$

Similarly we can calculate the errors in $\int_0^P VdP$. All the partial derivatives have been obtained in analytic form (the formulas are not given to save space). In the tables, the estimators for the standard deviations are given in parentheses. The meaning of these is the error associated with the errors in the experimental data, and they are specific for each of the methods of constructing the equation of state. The systematic error associated with a particular equation of state is determined by comparison with experiment.

Error calculations [5, 11, 31] for various compounds (MgO, α-, β-, γ-Mg_2SiO_4, Al_2O_3, CaO, diopside, spinel, pyrope, grossular, etc.) show that the standard deviation in $\int_0^P VdP$ does not usually exceed 0.5-1% at the temperatures and pressures of the upper and lower mantle. Similar errors are characteristic of the most reliable values for the standard thermodynamic functions tabulated in works of reference.

CONCLUSIONS

1. Basic thermodynamic specifications have been formulated for information on the equations of state for minerals as required in calculating chemical and phase equilibria over wide ranges in temperature and pressure.

2. The commoner methods of constructing the thermal equation of state for a solid have been compared and isothermal $P-V$ curves have been calculated for periclase, forsterite, and pyrope in the megabar pressure range. It is found that these methods and models give results in good agreement with one another (an exception is represented by the third-order Lagrange equation). The maximum discrepancy in pressure between the equations at 298 K and 1 Mbar is 7%, which corresponds to the errors of current methods of static and shock compression.

3. Comparison has been made on the basis of the temperature dependence of the various equations of state, and the sensitivity to the construction method has been established. The Murnaghan and Tait empirical equation are not applicable to describing high-temperature compression curves at pressures of $P \gtrsim K_0/4$. In certain cases (pyrope) the applicability may be restricted to much lower pressures. The compression curves for high temperatures defined in the quasi-harmonic approximation by potential methods in (42) and (49)-(52) and from the theory of elasticity with the Euler deformation measure of (58) are in good agreement with one another. At present, as experimental data are lacking, it is not possible to give preference to any one of these. The criterion here should be agreement with experimental data on the compressibility at high temperatures and pressures.

4. Various semiempirical equations of state have been used for periclase, forsterite, and pyrope in calculating $\int_0^P VdP$, which characterizes the isothermal dependence of the chemical potential on pressure. It is found that the numerical values of the integrals are virtually independent of the model and the method of constructing the equation of state. The calculations and the error estimates indicate that $\int_0^P VdP$ is determined with high accuracy, which considerably exceeds the accuracy of the $P-V-T$ data, and the values can now be tabulated in thermodynamic works of reference along with the standard thermodynamic functions. The monovariant curves for chemical and phase equilibria at very high P and T are constructed from the values of $\int_0^P VdP$, so we have a rigorous basis for reliability in such calculations.

5. Equations of state provide a basis for handling three major tasks in physicochemical simulation of mantle processes: 1) the construction of phase diagrams for multicomponent mineral systems, 2) the calculation of heat and volume effects from chemical and phase transformations at the P and T of the mantle, and 3) determination of standard thermodynamic functions from experimental

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