Equations of State of Compressed Gases for Thermodynamic Databases Used in Petrology

T. V. Gerya and L. L. Perchuk

Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: ltp@p1854.home.chg.ru
Received August 29, 1996

Abstract—Based on the ideas of L.D. Landau, the Gibbs thermodynamic potential \( G \) of compressed gas is examined as a function not only of temperature and pressure but also of the degree of ordering. The chosen ordering parameter \( X_{mol} \) (mole fraction of liquidlike particles) is determined from the condition \( G = f(P, T, X_{mol}) = \min \). The expression is also a generalized equation of state, which is valid in both two-phase and supercritical regions for polar (methane, water, and carbon dioxide) and nonpolar (argon) compressed gases. The least-square deviation involved in the description of the input data is 7–14 cal/mol for the Gibbs potential, 0.30–0.54% for volumes, 0.06–0.31 cal/mol/K for the entropy, and 0.35–0.51% for the pressure along a two-phase curve. This confirms the main idea of this paper that differences in the physical nature of intermolecular forces do not dramatically affect the form of a general equation of state for them. This equation shows good extrapolation properties in terms of both temperature and pressure and allows the reproduction of the results of independent high-pressure and high-temperature experiments with an accuracy sufficient for solving petrological problems.

INTRODUCTION

There is a great number of equations for describing, with varying accuracy, the thermodynamic properties of compressed gases (fluids). According to the pithy remark of Holloway (1987), "equations of state come in a bewildering variety of forms and complexities." Apparently, any attempt to append one more equation to this incredible multitude seems to be at least peculiar in itself. Nevertheless, we believe that the form of an equation of state and the number of empirical coefficients involved must be determined by the purpose of the equation. When a very high accuracy is desired in describing experimental data (for example, if the final accuracy should be of the same order as the accuracy of the experimental values used), the equation can include several parameters, and the number of empirical coefficients will be as large as a few dozen. The majority of such equations is based, in one way or another, on the equation of van der Waals, which is complicated by a required number of empirical (adjustable) parameters whose theoretical meaning is often far from clear. Brodholt and Wood (1993) commented that, because there is still no correct and justified equation of state for compressed gases, any extrapolation of their properties to elevated temperatures and pressures is very difficult.

Of the great number of equations currently used to describe the properties of fluids, a noteworthy technique is based on the corresponding state approach, which was pioneered by van der Waals. The method makes use of the \( P-T \) parameters at critical points (for example, Newton, 1935; Mel'nik, 1978; Holloway, 1987) and involves attaining a good correlation between the \( P-V-T \) properties of pure gases with the so-called normalized temperature, pressure, and volume:

\[
\tau_i = T/T_e, \quad \pi_i = P/P_e, \quad \varphi_i = V/V_e.
\]

Using this method, Mel'nik (1978) determined a linear dependence between the logarithm of the fugacity coefficient of gas \( i \) and the parameter \( \pi_i \). This allowed Mel'nik to predict the thermodynamic properties of many gases with errors of no more than 3–6% over wide extrapolation intervals of \( T \) and \( P \). Similar results were obtained by Perchuk (1973) on the basis of a linear extrapolation of the temperature functions for the molar volumes of several gases. Saxena and Fie (1987) applied the method of corresponding states to individual gases compressed under \( P-T \) conditions close to those in the Earth's core. The normalized parameters for argon, methane, oxygen, hydrogen, nitrogen, and carbon dioxide, which were calculated on the basis of experiments with shock waves, appeared to be in relatively good agreement with one another.

An interesting branch in studies of supercritical gases involves calculations of the constants for molecule association reactions (Gupta et al., 1992; Barelko et al., 1994). However, in spite of the obvious advances in the qualitative description of processes in supercriti-

\footnote{Notation: \( T \) = temperature, \( K \); \( P \) = pressure, \( b \); \( R \) = universal gas constant, 1.987 cal/mol/K; \( C_p \) = isobaric heat capacity, cal/grad; \( S \) = molar entropy, e.u.; \( V \) = molar volume, cal/bar; \( G \) = molar free Gibbs energy, cal/mol; \( F \) = molar Helmholtz free energy, cal/mol; \( \gamma_i \) = fugacity and fugacity coefficient of component \( i \), respectively; \( T_e \), \( P_e \), and \( V_e \) = temperature, pressure, and volume, respectively, at the critical point.
EQUATIONS OF STATE OF COMPRESSED GASES

Recent progress in computer engineering brought about an active development of numerical simulations of the structure and properties of compressed gases on the basis of the Monte Carlo technique (Kalinichev, 1986, 1991) and molecular dynamics (Belonosshko and Saxena, 1991; Brodholt and Wood, 1993). The molecular-dynamics models developed by Belonosshko and Saxena (1991) made it possible to approximate the results of molecular-dynamics modeling of gas properties by polynomials with a relatively small number of coefficients. The molar volumes calculated by Belonosshko and Saxena (1991) for some gases and their mixtures at $P > 5$ kbar agree satisfactorily with experimental data. However, showing limited accuracy, this equation found no use in calculating mineral equilibria at crustal $P$–$T$ conditions ($<5$ kbar) and, thus, could not be applied to calculations in databases. This led to the idea of the SUPERFLUID computer program (Belonosshko et al., 1992), which uses, in addition to the above-mentioned equations, equations of state for individual gases, based on traditional thermodynamic models, for the interval 1–5000 bar.

Our study is an attempt to develop an equation of state for compressed gases (fluids) proceeding from the thermodynamics of mixtures. The model should have good extrapolation properties and could be easily used in thermodynamic databases.

DERIVATION OF AN EQUATION OF STATE FOR FLUIDS FROM THE GIBBS POTENTIAL

A fluid exists in two distinct states (gas and liquid) below its critical point and becomes homogeneous above the point. The same relationships were detected in crystalline solutions with pronounced immiscibility regions, particularly in solutions with a variable ordering degree. In addition to two-phase (and more) equilibria, the theory of solid solutions examines intraphase equilibria. This concept claims that a phase can consist of two and more equilibrium components (subphases) in different structural states. The proportions of these subphases vary with temperature and pressure. This provides the basis for describing the thermodynamics of solid solutions. By analogy, this formalism can be used in developing the equation of state for a fluid.

Landau and Lifshits (1995, p. 572) proposed to express the thermodynamic Gibbs potential of a fluid as a function not only of temperature and pressure but also of its ordering, with the ordering parameter determined by the minimum of the potential. To introduce the ordering parameter, it is reasonable to assume that molecules of liquid can exist in two modes (liquid- and gaslike) at any $P$ and $T$, and these two states differ in the interaction energy with the medium. A transition from one state to the other can be expressed as a phase transition (boiling of liquid):

$$Liq = Gas,$$  \hspace{1cm} (1)

where $Gas$ is a molecule in the gaslike state and $Liq$ is a molecule in the liquidlike state. For brevity, we will refer to these molecules as liquidlike and gaslike ones. Along the boiling curve of a liquid, two equilibrium phases will coexist, which differ in the proportion of these molecules. Equilibrium (1) should be attained, in this case, both between the phases and within them. The boiling curve of a liquid is similar to the boundary of the immiscibility region of two phases in a solid solution, with each of the phases containing a certain amount of molecules of “the other type” up to the critical point. This is illustrated by Fig. 1, which was constructed on the basis of calculated equilibrium states for the molecules of aqueous fluid (see below). As can be seen from the plot, liquid water can contain gaslike molecules, and the coexisting gas bears liquidlike molecules. However, in our case, an important difference from a crystalline solution is the fact that molecules of different type can be transformed into one another according to reaction (1) in each of the phases, and the equilibrium relationships are uniquely determined by the temperature and pressure. This decreases the number of freedom degrees of the system, and, thus, $P$ and $T$ cannot vary independently along the liquid boiling curve, in contrast to these parameters on the immiscibility curve of a solid solution. Equilibrium (1) in a homogeneous solution is most similar to the ordering process in a solid solution, with the ordering being controlled by the temperature and pressure.

For a homogeneous fluid, equilibrium in accordance with reaction (1) can be written in the conventional form:

$$G = RT \ln (X_{Gas} / X_{Liq}) + \Delta G^{0}_{(1)} + \Delta G^{e}_{(1)} = 0,$$  \hspace{1cm} (2)

where $\Delta G^{0}_{(1)}$ and $\Delta G^{e}_{(1)}$ are the changes of the standard and the partial molar excess Gibbs energy for reaction (1), and $X_{Liq}$ and $X_{Gas}$ are the molar fractions of liquidlike and gaslike molecules, $X_{Liq} + X_{Gas} = 1.$ Here and below, the term standard refers to the properties of a gas and
liquid at $X_{Gas} = 1$ and $X_{Liq} = 1$, respectively. The integral molar Gibbs energy of fluid $G^m$ will be subject to the condition

$$G^m = G_{Liq}^0 + RT[X_{Gas}\ln(X_{Gas}) + X_{Liq}\ln(X_{Liq})] + \Delta G_{(1)}^0,$$  \hspace{1cm} (3)

where $G_{Liq}^0$ is the standard molar Gibbs energy of a substance consisting only of liquidlike molecules, and $\Delta G_{(1)}^0$ is the excess molar energy of mixing liquidlike and gaslike molecules. Expression (3) is the $P-T-X$ equation of state for a gas–liquid system.

For further thermodynamic analysis, it is convenient to express the last two terms in equation (3) as

$$G^* + X_{Gas}\Delta G_{(1)}^0 = G_p + G_T,$$  \hspace{1cm} (4)

where

$$G_p = \int_{P_0}^P \left[\Delta V_{(1)}^0 X_{Gas} + V^* \right] dP,$$

$$G_T = X_{Gas}[\Delta H_{(1)}^{00} - T\Delta S_{(1)}^{00}] + H^p - TS^0$$

$$\begin{align*}
  &\int_{T_0}^T [\Delta C_P^0 X_{Gas} + C_p^*] dT \\
  &- T \int_{T_0}^T [\Delta C_P^0 X_{Gas} + C_p^*]/T dT,
\end{align*}$$

in which $P_0 = 1$ bar; $T_0 = 298.15$ K; $\Delta V_{(1)}^0$ and $V^*$ are the standard volume change of reaction (1) and the excess volume of the fluid, respectively, both as functions of $P$ and $T$; $\Delta H_{(1)}^{00}$ and $\Delta S_{(1)}^{00}$ are the standard enthalpy and entropy changes of reaction (1) at $P_0$ and $T_0$; $H^p$ and $S^0$ are the contributions to the excess enthalpy and entropy, respectively, not related to $V^*$ at $P_0$ and $T_0$; and $\Delta C_P^0$ and $C_p^*$ are the changes of the standard heat capacity for reaction (1) and the excess heat capacity of the fluid as a function of temperature at $P_0$.

To reveal the form of the term $G_p$ in (4), let us assume that the volume of one mole of matter consisting only of gaslike molecules can be expressed as two terms: the conventional molecular volume $V_r$ and the free volume $V_f$ (Prigogine and Defay, 1954). Then

$$V_{Gas}^0 = V_r + V_f = V_s + RT/P.$$  \hspace{1cm} (5)

The volume of one mole of substance that consists only of liquidlike molecules will be determined by only the molecular volume:

$$V_{Liq}^0 = V_s.$$  \hspace{1cm} (6)

Hence, the standard volume increment of reaction (1) is

$$\Delta V_{(1)}^0 = V_{Gas}^0 - V_{Liq}^0 = RT/P.$$  \hspace{1cm} (7)

Taking into account (5) and (6), the total volume of a mixture consisting of liquidlike and gaslike molecules will be

$$V = X_{Gas} V_{Gas}^0 + X_{Liq} V_{Liq}^0 + V^*$$

$$= V_s + X_{Gas}RT/P + V^*.$$  \hspace{1cm} (8)

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

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

where $\beta$ is the correction for the molecular volume; i.e., $\beta = V_s$, and $\lambda = \text{const}/V^2$ is the correction for the attractive forces between the molecules. A correction for $\lambda$ can be introduced into (7)

$$V^* + X_{Gas}\Delta V_{(1)}^0 = V^* + X_{Gas}RT/P$$

$$= X_{Gas}RT/(P + \lambda).$$  \hspace{1cm} (9)

Appropriately, $\lambda$ should depend on the average distance between molecules in the gas. Taking into account the volume difference of reaction (1), this distance should be a function of $X_{Liq}$. As the external pressure decreases, the volume of the system approaches that of an ideal gas, $RT/P$, and both $X_{Liq}$ and $\lambda$ tend to zero. As the pressure increases, $X_{Liq}$ and $\lambda$ increase. Hence, $\lambda$ can be expressed as a function of $X_{Liq}$ in the form

$$\lambda = \lambda_1 X_{Liq} + \lambda_2 X_{Liq}^2 + \ldots + \lambda_n X_{Liq}^n,$$  \hspace{1cm} (10)

where $\lambda_1, \lambda_2, \ldots, \lambda_n$ are coefficients, which are independent of $X_{Liq}$ and characterize variations in $\lambda$ with change in the external parameters of the system. Integrating (8) in accordance with (4) yields the following equation for $G_p$:

$$G_p = X_{Gas}RT\ln[(P + \lambda)/P_0].$$  \hspace{1cm} (11)

In deriving equation (10), the assumed standard state was $\lambda = 0$.

The temperature and concentration functions of the integral Gibbs energy ($G_T$) for mixing components $Liq$ and $Gas$ in fluid can be written, taking into account (4) and using the Margules series, in the form:

$$G_T = X_{Gas}[\Delta H_{(1)}^{00} - T\Delta S_{(1)}^{00}]$$

$$+ \Delta C_P^0[T - T_0 + T\ln(T/T_0)]]$$

$$+ W_1^G X_{Gas}X_{Liq} + W_2^G X_{Gas}X_{Liq}^2 + \ldots + W_n^G X_{Gas}X_{Liq}^n,$$
where $\Delta C_p^{00}$ is the standard heat capacity difference for reaction (1) under $P_0$ and $T_0$, and $W$ are Margules' parameters.

To describe the energy $G_{\text{Liq}}^0$ in (3) for a substance consisting only of liquidlike molecules, it is reasonable to examine separately its two functions: one of temperature and one of pressure.

The baric function for the energy of molecules of a substance in a condensed state is controlled by their interaction. At 0 K, it can be derived from the potential energy as a function of the average volume $V_s$ occupied by these particles. A function of this form can be described by a variety of semiempirical equations. The function can be expressed through the volume occupied by one molecule of the substance; the form of this function is similar to that of the Lennard–Jones potential for coupled intermolecular interaction (6 : 12):

$$E_V = \frac{\alpha}{V_s^4} - \frac{\beta}{V_s^2}, \quad (12)$$

where $E_V$ and $V_s$ are the potential energy and the volume, respectively, and $\alpha$ and $\beta$ are parameters that characterize repulsive and attractive forces, respectively. Hence, the pressure can be determined as

$$P = -\frac{\partial E_V}{\partial V_s} = 4\alpha/V_s^4 - 2\beta/V_s^3, \quad (13)$$

A gas–liquid system under $P > 0$, $4\alpha/V_s^4 > 2\beta/V_s^3$ is dominated by attractive forces. Hence, equation (13) can be replaced by the expression

$$P = \frac{\alpha}{V_s^4} - \lambda_s, \quad (14)$$

where $\lambda_s$ is the correction for attractive forces and $\alpha$ is the parameter characterizing the repulsive forces. Evidently, $\lambda$ approaches $\lambda_s$ with $X_{\text{Liq}}$ tending to one, because both of the corrections characterize the same forces between molecules. Then, in accord with (9)

$$\lambda_s = \lambda_1 + \lambda_2 + \ldots + \lambda_n, \quad (15)$$

Expressing the volume through pressure, we obtain

$$V_s = (\alpha_1)^{1/5}/(P + \lambda_s)^{1/5} = \Theta/(P + \lambda_s)^{1/5}, \quad (16)$$

where $\Theta = (\alpha_1)^{1/5}$. An expression for the change in the Gibbs energy as a function of pressure at 0 K can be easily derived from (16):

$$G_s^P = (5\Theta/4)[(P + \lambda_s)^{4/5} - (P_0 + \lambda_s)^{4/5}]. \quad (17)$$

The thermal function of $G_{\text{Liq}}^0$ for molecules in a liquidlike state appears in (3) at temperatures above 0 K.

As test calculations indicate, the function is best described by an equation analogous to that used in solid-state physics for describing thermodynamic potential and is based on the Bose–Einstein distribution (Landau and Lifshits, 1995, p. 186). Taking this into account, one can write (Bergya et al., 1991)

$$G_s^t = \sum_{i=1}^{n} (c_i)_s RT \ln \left[ 1 - \exp \left( -\frac{(\Delta G)^{i}_s}{RT} \right) \right], \quad (18)$$

where $n$ is the number of terms of $C_p$ expansion into a series, $(c_i)_s$ is the number of freedom degrees for the $i$th term of the expansion, and $(\Delta G)^{i}_s$ can be written, in view of (17), as

$$(\Delta G)^{i}_s = (\Delta H)_s^{i} + 5\Theta_i/(4[(P + \lambda_s)^{4/5} - (P_0 + \lambda_s)^{4/5}]), \quad (19)$$

where $(\Delta H)_s^{i}$ and $\Theta_i$ are the differences of the enthalpy and the parameter of the repulsive potential, respectively, related to the $i$th term of the heat capacity expansion in a series as a function of temperature.

The final expression for the molar Gibbs energy, $G_{\text{Liq}}^0$, for liquidlike molecules can be now written in the form

$$G_{\text{Liq}}^0 = H^0 - T S^0 + \sum_{i=1}^{n} (c_i)_s RT \ln \left[ 1 - \exp \left( -\frac{-(\Delta G)^{i}_s}{RT} \right) \right] - RT \ln \left[ 1 - \exp \left( -\frac{-(\Delta H)^{i}_s}{RT} \right) \right] \quad (20)$$

$$+ 5\Theta_i/4[(P + \lambda_s)^{4/5} - (P_0 + \lambda_s)^{4/5}],$$

where $H^0$ and $S^0$ are the molar enthalpy and entropy of the substance in a liquidlike state, respectively, at $T_0$ and $P_0$.

Expressions (4)–(20) reveal the meaning of equation (3), which is the $P$–$T$–$X$ equation of state of a gas–liquid system. To calculate the $P$–$T$–$X$ properties of such a system, one can first calculate, by equation (2), the equilibrium $X_{\text{Liq}}$ value corresponding to the minimum Gibbs energy in (3); i.e., $G^m = \min$. An expression for the difference in the standard and the excess Gibbs energy in (2) can be derived from equation (3) and the Gibbs–Duhem equation

$$\Delta G_{(1)} + \Delta G_{(1)}^e = -\partial G^m/\partial X_{\text{Liq}} -$ RT $\ln (X_{\text{Gas}}/X_{\text{Liq}}). \quad (21)$$

The applicability of the expressions to compressed gases was tested using the tabulated thermodynamic properties of H$_2$, O$_2$, CO$_2$, CH$_4$, and Ar. The purpose of the tests was to describe the thermodynamic properties of gases and liquids over wide $P$ and $T$ intervals with desirable accuracy, which should be high enough to utilize the equations of state for gases in bases of consis-
tent thermodynamic data on phase equilibria. For the
Gibbs potential, the accuracy corresponds to the mean
square error of description (±20 cal/atom). Our tests of
equations (2), (3) demonstrate that desirably low
description errors can be attained in equations (3) of
relatively simple form, with no more than 14 paramet-
ers:

\[ G^m = H_0 - TS_0 + RT \left( X_{liq} \ln X_{liq} + X_{gas} \ln X_{gas} \right) + X_{gas} \Delta G^{00} + X_{gas} \Delta H_{liq} W_{liq}^G + X_{gas} \Delta H_{gas} \ln(\lambda + P) + c_1 RT \ln \left( 1 - \exp(-\Delta H_{gas}/RT) \right) + c_2 RT \ln \left( 1 - \exp(-\Delta H_{liq}/RT) \right) + \Theta B \left( c_1 + c_2 \right) \left( \Delta H_{liq} / T \right) \] (22)
\[ \times \exp(-\Delta H_{gas}/RT_0) / \left( 1 - \exp(-\Delta H_{gas}/RT_0) \right) \right) + RT \ln \left( 1 - \exp(-\Delta H_{liq}/RT_0) \right) \],

where

\[ \lambda = \lambda_2 \lambda_2, \]
\[ \Delta G_{gas} = \Delta H_{gas} + \Delta \Theta B, \]
\[ B = \frac{5}{4} \left[ \left( P + \lambda_2 \right)^{4 \beta} - \left( P_0 + \lambda_2 \right)^{4 \beta} \right], \]
\[ X_{gas} + X_{liq} = 1, \]
\[ \Delta G^{00} = \Delta H^{00} - T \Delta S^{00} \]
\[ + \Delta C_p^{00} \left( T - T_0 - T \ln \left( T/T_0 \right) \right). \]

In calculating parameters in (22) for H$_2$O, CO$_2$,
CH$_4$, and Ar, we used tabulated data only for experi-
mentally examined P-T intervals. A more detailed
account of our knowledge of the properties of each gas
will be given below. The tables report calculated
parameters of equation (22) obtained by a cyclic treat-
ment of databases on H$_2$O, CO$_2$, CH$_4$, and Ar on
the basis of the nonlinear least-squares technique.
The main criterion used in the calculations of the para-
eters was the minimum of the mean square error in
inverted calculations of the Gibbs potential, volume,
and entropy. In addition, we controlled the values of
boiling pressures ($P_{boiling}$), which were calculated for a
given temperature at the gas–liquid equilibrium curve
below the critical point. The mean square errors of
description and the maximum deviations of the above-
mentioned thermodynamic data from the input data are
listed in the table.

P–V–T PROPERTIES OF WATER

There are a great number of equations that describe,
with varying accuracy, the thermodynamic properties
of water. As was mentioned above, all of them are based
on experimental data, whose accuracy depends on the
equipment used and the method employed in determin-
ing the physical properties (volume, density, sound
velocity, etc.) of H$_2$O at elevated P–T parameters. The
thermodynamic processing of these data is the basis of
derived equations of state for water, which are utilized
in petrology solely in the form of P–V–T relationships (Pechuk, 1973; Mel’nik, 1978; Bulakh and Bulakh,
1978; Burnham et al., 1969; Helgeson and Kirkham,
1974; Holloway, 1977; Kerrick and Jackobs, 1981;
Halbach and Chatterjee, 1982). The development of
these equations involves searches for the most suitable
equations describing, with petrologically reasonable
accuracy (which is, for example, 0.5% for $V_{liq}$), the
dependencies of the volume of water on temperature
and pressure. In fact, in describing deviations of H$_2$O
properties from those of an ideal gas one takes into
account the increment of the Gibbs free energy caused
by intermolecular electrostatic interactions. These
interactions are functions of the geometry of mole-
cules, their interatomic distances, and the polarity
degrees. A particular role is assigned to hydrogen, more
specifically, to its bond with oxygen in the supercritical
water structure (Gupta et al., 1992).

In the petrological and geochemical literature (for
example, Holland and Powell, 1990), the thermody-
namic treatment of experimental data on the changes in
water volume at elevated P and T is based on the Gibbs
potential $G = f(P, T)$. Fairly comprehensive reviews of
experimental data and equations of state for water,
which were derived from these data, were published by
Pechuk (1973), Mel’nik (1978), Bulakh and Bulakh
(1978), Haar et al. (1984), Hill (1990), Saul and Wagner
(1989) and many other scientists. These data may be
supplemented with elegant experimental works by
Brodholt and Wood (1994), who measured the molar
volume of water over the temperature interval from 930
to 1600°C and pressures from 9.5 to 25 kbar in syn-
thetic fluid inclusions in corundum.

Based on comprehensive critical analysis, Mel’nik
(1978) proposed to use the experimental results of
Kennedy (1950) and Holster (1954) as the only refer-
ce points for the intervals 1–1000 bar and 400–550 K,
the data of Jusa (1966) for 1000–5000 bar and 10,000–
15,000 bar at 400–1500 K, and those of Koster and
Frank (1969) for 5–10 kbar at 400–1500 K.

In addition to studies of the P–V–T properties of
water in application to petrological and geophysical
problems, many works were devoted to the derivation
of a general equation of state for water in application to
technological tasks. Thermal physicists and physical
chemists “competitively” derive more and more precise
equations of state, as, for example, in the above-men-
Calculated constant for equation (22) of the Gibbs free energy of gases

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Argon</th>
<th>Methane</th>
<th>Carbon Dioxide</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^{00}$</td>
<td>cal/mol</td>
<td>247.62019</td>
<td>1479.8541</td>
<td>4925.8228</td>
<td>10717.4</td>
</tr>
<tr>
<td>$\Delta S^{00}$</td>
<td>cal/mol/K</td>
<td>30.374805</td>
<td>28.631362</td>
<td>33.086146</td>
<td>29.2557</td>
</tr>
<tr>
<td>$\Delta C_p^{00}$</td>
<td>cal/mol/K</td>
<td>0.1839337</td>
<td>-0.345089</td>
<td>-2.400152</td>
<td>-5.13570</td>
</tr>
<tr>
<td>$W_1^{II}$</td>
<td>cal/mol</td>
<td>-5467.852</td>
<td>-4982.556</td>
<td>-4985.791</td>
<td>-6882.22</td>
</tr>
<tr>
<td>$W_1^q$</td>
<td>cal/mol/K</td>
<td>9.1261191</td>
<td>7.4123812</td>
<td>8.8117827</td>
<td>-2.79764</td>
</tr>
<tr>
<td>$W_1^{CP}$</td>
<td>cal/mol/K</td>
<td>3.9236457</td>
<td>1.5429817</td>
<td>0</td>
<td>1.21559</td>
</tr>
<tr>
<td>$H_0$</td>
<td>cal/mol</td>
<td>1224.7253</td>
<td>3137.3241</td>
<td>3550.8439</td>
<td>340.861</td>
</tr>
<tr>
<td>$S_0$</td>
<td>cal/mol/K</td>
<td>6.6004625</td>
<td>15.925436</td>
<td>17.917433</td>
<td>1.05267</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>cal</td>
<td>15.232284</td>
<td>580.55343</td>
<td>1350.55</td>
<td>1096.26</td>
</tr>
<tr>
<td>$\Delta \Theta_f$</td>
<td>cal/bar$^{45}$</td>
<td>0.0387218</td>
<td>0.6159146</td>
<td>0.5724886</td>
<td>0.05910</td>
</tr>
<tr>
<td>$\Theta_s$</td>
<td>cal/mol/bar$^{45}$</td>
<td>0.4177045</td>
<td>1.0182855</td>
<td>2.1126283</td>
<td>7.23575</td>
</tr>
<tr>
<td>$\lambda_2$</td>
<td>bar</td>
<td>8385.2962</td>
<td>5444.5446</td>
<td>6551.3123</td>
<td>6208.86</td>
</tr>
<tr>
<td>$c_2$</td>
<td></td>
<td>2.0115894</td>
<td>4.3424714</td>
<td>5.7876907</td>
<td>0.31482</td>
</tr>
</tbody>
</table>

| $\sigma V$ | %            | 0.30        | 0.54        | 0.50        | 0.48       |
| $\Delta V^{max}$ | %          | 2.01        | 2.59        | 3.27        | 2.27       |
| $\sigma G$ | cal/mol      | 6.6         | 14.3        | 10.3        | 12.2       |
| $\Delta G^{max}$ | cal/mol     | 24.3        | 45.3        | 29.6        | 38.4       |
| $\sigma S$ | cal/mol/K    | 0.06        | 0.31        | 0.11        | 0.17       |
| $\Delta S^{max}$ | cal/mol/K   | 0.56        | 1.28        | 0.82        | 0.86       |
| $\sigma P_{LG}$ | %           | 0.39        | 0.35        | 0.51        | 0.46       |
| $\Delta P_{LG}^{max}$ | %      | 1.39        | 1.41        | 1.16        | 1.99       |

tioned papers by Saul and Wagner (1989) and Hill (1990). In both of these papers, the equation of state for water is derived based on the Helmholtz potential $F = f(V, P)$. Both papers, particularly the latter one, present detailed reviews of preexisting experimental and theoretical works dealing with thermal physics. This largely simplifies our task, particularly in comparing our data with the results obtained by other scientists. It is pertinent to recall that Saul and Wagner (1989) empirically derived 58 coefficients for the equation of state for water (not counting the coefficients in the equation for the water heat capacity) for the $P-T$ interval from the ice melting curve to 1000°C and 250 kbar. As the authors claim, the accuracy of fitting of their equation against 17000 primary measurements corresponds to the experimental accuracy. However, reliable systematic experimental data are available only for pressures below 10 kbar. Extrapolations up to 250 kbar were accomplished by Saul and Wagner mainly based on experiments with shock waves and by the introduction of many new parameters (58 new as opposed to the 35 original ones) in the equation of state. The equation of state proposed by Hill (1990) describes, with the experimental accuracy, water properties up to 1000°C and 10 kbar and utilizes 82 coefficients (also not counting the heat capacity equation).

All of the above-mentioned methods for deriving the equation of state for water are largely based on the purely statistical processing of experimental data and the use of certain thermodynamic potentials. There are no theoretical models for deriving the equations of state, a fact significantly hampering extrapolations to the high-pressure region of water state. This seems to be the reason that triggered the recent development of techniques for the numerical simulation of the structure and properties of pure water. The approaches are based on Monte Carlo simulations (Kalinschek, 1986, 1991) and methods of molecular dynamics (Belonoshko and Saxena, 1991; Brodholt and Wood, 1993).

Investigations into the structure of water up to a pressure of 1 kbar and temperatures up to 500°C demonstrate (Gorbaty and Demianets, 1983) that near-critical fluctuations remain at elevated $P-T$ conditions (above the critical point). In the supercritical region, there are space fluctuations that correspond to the liquidlike and the gaslike state. These data justify the choice of our model approach. The principal difference of our equation (22) from other equations of state...
The diagram illustrates the method for determining the mole fraction of liquidlike molecules in fluid on the basis of the Gibbs energy of the gas–liquid system. The diagram is calculated for water under a pressure of 86 bar.

involves the necessity of calculating equilibrium $X_{H}$ by equation (2). As was demonstrated above, the calculations are based on the idea of determining the minimum Gibbs energy. A graphical variant of the procedure for equilibrium (1) in liquid, at the phase transition point, and in gas is illustrated by Fig. 2. At a temperature of 250°C, the minimum Gibbs energy ($G^m - G_{Liq}^o$) corresponds to the mole fraction of liquidlike water $X_{Liq} = 0.68$. At the point of two-phase equilibrium, there are two equivalent minima in the Gibbs energy, ($G^m - G_{Liq}^o = -890$ cal/mol. Each of the coexisting phases contains different mole fractions of liquidlike molecules: $X_{Liq} = 0.62$ in the liquid phase, and $X_{Liq} = 0.05$ in the equilibrium gas phase. In the gas-phase field, which corresponds to the minimum Gibbs energy at 350°C, $X_{Liq} = 0.04$ (i.e., nearly the same value). The procedure makes it possible to use the minimized Gibbs energy to calculate the equilibrium $X_{Liq}$ at specified $P$-$T$ conditions, which is the basis of the method described here. Calculated isotherms for baric functions of $X_{Liq}$ in divariant fields and the two-phase (univariant) region are shown in Fig. 3a. As can be seen from this figure, the mole fraction of molecules in the liquidlike state notably varies with temperature and pressure in pure water fluid. Above the critical point and, particularly, under very high pressures, the fluid is strongly dominated by liquidlike molecules, whose percentage increases with decreasing temperature. Figures 3b and 3c compare the mole fraction of molecules in the liquidlike state, $X_{Liq}$, and the mole fraction of hydrogen bonds, $X_{H}$, as functions of temperature, which were calculated by Gorbaty and Kalinichov (1995) on the basis of experimental data (the association of molecules in aqueous fluid is mainly determined by hydrogen bonds). Hence, the similar behavior of $X_{H}$ and $X_{Liq}$ and the high correlation coefficient ($r = 0.94$) between them suggest that our approach makes it possible to reveal the actual association degree of molecules in aqueous fluid.

The application of the equation of state for pure water to thermodynamic processing of experimental data on equilibria of water-bearing minerals in the presence of excess aqueous fluid is far from being always correct because of the high solubilities of the solids in fluid. For example, the application of any equation of state for water to the thermodynamic description of hydration–dehydration reactions in systems with silicates results in systematic discrepancies with experimental data, particularly in the low-pressure region. This can be illustrated by the calculations performed by Berman (1988, Fig. 42) with reactions including phlogopite and muscovite:

$$
M_s^{2)} = S_a + C_rn + H_2O,
$$
$$
M_s + Q_tz = S_i + S_a + H_2O,
$$
$$
Q_tz + M_s + P_hl = S_a + C_rn + H_2O,
$$
$$
A_nn + O_2 = S_a + M_ag + Q_tz + H_2O,
$$
$$
P_hl + Q_tz = 3E_n + S_a + H_2O.
$$

The last reaction, which describes the development of the charnockite assemblage after biotite gneiss, displays discrepancies between data for moderate pressures (about 0.3 kbar), i.e., values that are well reproducible in experiments (Wood, 1976; Wones and Dodge, 1977). This predetermines incorrect results in attaining consistency in the thermodynamic constants for minerals in bases of thermodynamic data. Apparently unrealistic values of $P_hl$ and $A_nn$ activities were obtained by calculating the properties of the biotite solid solution on the basis of experimental data on the stability of the phlogopite-annite solid solution as a function of temperature and oxygen fugacity in the reaction $A_nn + O_2 = S_a + M_ag + Q_tz + H_2O$ (Wones and Eugster, 1965). Even the introduction of corrections into the model for the activity of this solid solution (Marakushch, 1968; Perchuk and Ryabchikov, 1976) did not diminish the large deviation of this solution from ideality, a state confirmed by numerous experimental data (for example, Perchuk and Lavrent'eva, 1983) on equilibria of biotite with garnet, cordierite, and some other minerals.

In the ideal case, a database is desired that would take into account the solubilities of silicates in fluid for systems of different bulk chemical composition. Theoretically, this could be accomplished, but in actual practice, it would be very difficult to use such a database for calculating the activity of water in fluid in equilibrium with rocks of various modal composition. This was one of the considerations that led us to revise the equation of state for water in the search for an efficient model.

\[^2\] Mineral symbols: $A_nn$ = anatite, $C_rn$ = corundum, $E_n$ = enstatite, $M_ag$ = magnetite, $M_s$ = muscovite, $Q_tz$ = quartz, $P_hl$ = phlogopite, $S_a$ = sanidine, $S_i$ = sillimanite.
that could be easily applicable to any system with relatively high mineral solubilities in free fluid. Evidently, such a model should have not only a clear physical meaning but also a simple analytical expression for the equation of state. The equation of state derived above for compressed gases (fluids) largely meets these requirements. In deriving mixing rules for this equation, one should be aware that \(X_{\text{Liq}}\) for a fluid of complex composition (for example, aqueous fluid with salts) can significantly differ from that for the pure system at given \(P\) and \(T\). In this case, the activity of water can be calculated in terms of ternary solution (\(X_{\text{Liq}} + X_{\text{Gas}} + X_{\text{Salt}} = 1\)).

**Input Data and Accuracy**

We created a database for the calculations of parameters in the equation of state for water on the basis of tabulated thermodynamic properties, which were calculated by the equation of Saul and Wagner (1989). The equation was proved to show a high accuracy against experimental data over the intervals 0–1000°C and 1–10,000 bar. Figures 4a–4c, and the table illustrate the fairly good fits of the volume, Gibbs energy, and entropy of water at different isotherms. Figures 5a and 5b demonstrate the fits between the initial and calculated data along the line of water–vapor phase transition. It should be mentioned that the position of the phase-transition line and of the critical point in the \(P-V-T\) space (Figs. 5a, 5b) were also calculated by equation (22) under the conditions of the minimum of the Gibbs energy and its equality in the coexisting liquid and gas phases (Fig. 2). Calculated \(X_{\text{Liq}}\) values in the gas and liquid coexisting along the two-phase curve are given in Fig. 5c. Significant errors were detected only for the volume of the gas phase in the proximity of the critical point (Figs. 4a, 5b), which lies, according to our calculations, 25°C higher than the experimental point (Fig. 5b). In calibrating equation (22), we deliberately excluded the critical region from the database, because all our attempts to obtain a good description of this region resulted in a strong decrease in the quality of the description for other \(P-T\) parameters. The problems encountered in describing gas volumes within the critical region have long been known and are not typical of either water fluid or any equation of state. Most scientists use here so-called switch functions to improve the description in the narrow \(P-V-T\) regions without disturbing the continuity of the functions (for example, Hill, 1990).

The extrapolation properties of our model were tested by comparison with high-pressure and high-temperature experimental results that were not involved in the data processing. The smallest deviations were determined with the experimental data of Brodholt and Wood (1994), who measured the molar volume of water in synthetic fluid inclusions in corundum. These discrepancies are practically always within the experimental errors. The same holds for the experimental data

Fig. 3. Variations in the mole fraction of liquid-like molecules with temperature and pressure. (a) Calculated isotherms for the baric function of the mole fraction of liquid-like molecules in aqueous fluid up to a pressure of 10 kbar. (b) Variations in the mole fraction of liquid-like molecules in aqueous fluid with temperature at a pressure of 1 kbar (line), symbols show variations in the mole fraction of hydrogen bonds \(X_{\text{H}}\) calculated by Gorbaty and Kalinichev (1995) on the basis of experimental data. (c) A positive correlation between the mole fraction of liquid-like molecules and the mole fraction of hydrogen bonds, \(r = 0.94\). Symbols in Figs. 3b and 3c indicate data obtained by various methods: (1) X-ray diffraction, (2) infrared absorption spectra, (3) same, data of Franc and Roth (1967).
of Bridgeman (1942) for the temperature range from 25 to 175°C and pressures of 10–34 kbar. Larger deviations were revealed with the shock-wave adiabatic experiments of Walsh and Rice (1957) and Lysenga et al. (1982). Considering them, it is important to stress that the volume of gas, as well as the pressure and enthalpy, are approximately evaluated in shock-wave experiments that use the Hugoniot relationship under the presumption that the shock wave has an “ideal shape.” In the strict sense, the change in the compressibility of gases and liquids in a shock wave are not always determined by their PVT properties. The temperature can sometimes be estimated indirectly, from the equation

$$dT = 1/C_p(dh - [v - (\partial V/\partial T)_p dP])$$

along the line connecting a series of states whose $P$, $V$, and $h$ are known. This was the technique applied by Walsh and Rice (1957) for evaluating the specific heat and the derivative of volume with respect to temperature under $P = \text{const}$. Walsh and Rice extrapolated, although not completely correctly, the $(\partial V/\partial T)_p$ derivative obtained from Bridgeman’s (1942) data for 175°C; i.e., Walsh and Rice deliberately ignored its temperature dependence. As a result, the temperature became equal to 3147°C at $P = 450$ kbar. Hence, the equation of state for water derived by Rice and Walsh (1957) for the ultrahigh-pressure region is not absolutely correct in the sense of the methods by which it was obtained. This was also confirmed by later shock-wave experiments (up to 1 Mbar) with a temperature control behind the shock wave (Lysenga et al., 1982). As these measurements indicated, the values obtained by Rice and Walsh are overrated by a few hundred grades, and their equation of state for water is erroneous. Hence, we prefer the equation of Mitchell and Nellis (1982), being aware that the accuracy of any experiments with shock waves is much lower than that of direct water volume measurements by conventional methods. A comparison between our data and the results of Belonoshko and Saxena (1991) is illustrated by Fig. 7: over the whole $P$-$T$ interval, the difference between the volume values calculated with equation (22) and estimated by methods of molecular dynamics are within the errors of the latter method. In Fig. 8, the water volume calculated by the equation of Saul and Wagner (1989) is compared with analogous values obtained by extrapolations with our equation (22). Both equations yield nearly identical results up to a pressure of 100 kbar and somewhat different values at higher pressures. Because Saul and Wagner calibrated their equation against the results of high-pressure experiments, the comparison provides further evidence for the good extrapolation characteristics of equation (22). The small discrepancies in the high-pressure region can be attributed to the excessive “rigidity” of the Lennard–Jones potential used in equation (12).
Fig. 5. Diagram comparing the pressures and molar volumes of H₂O along the line of phase transition. Solid lines show data calculated by equation (22) and coefficients from the table; dashed lines present tabulated data from (Saul and Wagner, 1989).
(a) Pressure; (b) molar volumes; (c) calculated mole fractions of liquidlike molecules in coexisting liquid and vapor.

Fig. 6. Diagram comparing the molar volume of H₂O at high pressures and temperatures obtained experimentally and calculated.
(1) Experimental data of Brodholt and Wood (1994), (2) experimental data of Bridgeman (1942), (3) data on the shock adiabat of water (Mitchel and Nellis, 1982), (4) same, data of Rice and Walsh (1957).

Fig. 7. Isotherms of changes in the H₂O molar volume up to the pressure 1000 kbar.
Dashed lines denote P–V–T properties of water modeled by molecular dynamics methods (Belonosshko and Saxena, 1989). Solid lines show calculations by equation (22) and coefficients from the table.

Fig. 8. Diagram comparing calculated data on the H₂O molar volume at pressures up to 200 kbar.
(1) Calculations by the equation of Saul and Wagner (1989), (2) calculations by equation (22) and coefficients from the table.
**P–V–T PROPERTIES OF ARGON**

Argon is a thoroughly studied gas, which has often been used to test various equations of state. In creating the database that will be used to calculate the parameters for the equation of state of argon, we utilized tables of thermodynamic properties calculated with the equation of state derived by Stewart and Jacobsen (1989). It was proved that this equation fits well experimental data over the intervals from −175 to 1000°C and 1–10000 bar. The authors included 30 empirical parameters in the equation, which is an expression for the Helmholtz energy of argon at specified density and temperature. As is evi...
Fig. 11. Isotherms of the basic functions for the molar thermodynamic parameters of carbon dioxide. Solid lines present data calculated by equation (22) and coefficients from the table, dashed lines are the data of Altunin (1975). (a) Volume, (b) Gibbs free energy, (c) entropy.

Fig. 12. Diagram comparing calculated data on the CO₂ molar volume at pressures up to 8 kbar (solid lines) with experimental results (crosses).
(a) Diagram calculated on the basis of the experimental data of Tsuklis et al. (1969); (b) diagram calculated on the basis of the experimental data of Shmonov and Shmulovich (1974).

Temperature is slightly overrated. The deviations of the Gibbs energy in the critical region are also relatively small.

**P–V–T Properties of Methane**

Reliable experimental data on the volume and heat capacity of methane are available for the intervals from −175 to 400°C and 1–10,000 bar, i.e., the limits within which we calculated parameters for equation (22). The input data were compiled from tables of thermodynamic properties published by Sychev et al. (1979). The high accuracy of the data was validated by their good fit with the experimental values. The original equation of state involves 54 empirical parameters in the expression for the compressibility coefficient and 17 parameters in the heat capacity equation. The errors (Figs. 10a–10c, table) appear to be generally larger than in the case of water and argon, but they do not exceed 10–15 cal when recalculated per one atom.
field. The deviations in the critical region are analogous to those described above for water, argon, and methane. The discrepancies with high-pressure experimental data (Figs. 12a, 12b) are usually larger but not systematic. Considerable volume overestimates (by 1.5–2.0%) were encountered only at $T = 600–700^\circ\text{C}$ and $P = 6–8$ kbar. There, the experimental isotherms have a weak bend (Fig. 12b), which was not observed in the case of the other gases. Because of this, the discrepancies can be accounted for by experimental errors. The extrapolation of the equation of state for carbon dioxide to high pressures (Fig. 13) is in good agreement with shock-wave adiabatic experiments.

**CONCLUSION**

The model derived for the continuous transformation of fluid from the gas to the liquid state proved to be an efficient tool in application to such very different gases as methane, argon, water, and carbon dioxide. The mean-square error of the description of the original data for all of the gases appeared to be relatively low: 7–14 cal/mol for the Gibbs potential, 0.30–0.54% for the volume values, 0.06–0.31 cal/mol/K for the entropies, and 0.35–0.51% for the pressures along the two-phase curves. This means that the differences in the physical nature of intermolecular interaction forces in different gases do not preclude the use of our approach in deriving a uniform equation of state for these gases. Our equation (22) is characterized by good extrapolation properties with respect to both temperature and pressure and yields relatively good fits with the results of independent high-pressure and high-temperature experiments.

Figure 14 illustrates the extrapolation properties of the equation of state. It follows that our equation is the first equation of state for fluid that is based on a simple thermodynamic model and enables one efficiently to describe and extrapolate the $P$–$V$–$T$ properties over wide intervals of temperature and pressure.

This demonstrates that our model can be successfully used in creating thermodynamic databases for mineral systems. Of course, the model must be adapted to fluid of complex composition by means of the introduction of specified mixing rules. Because of the small number of coefficients in equation (22) and because they have a clear physical meaning, the development of such rules seems to be a feasible task, which will be carried out in our later studies.

**ACKNOWLEDGMENTS**

This work was inspired by S.I. Tkachenko (Institute of Experimental Mineralogy, Russian Academy of Sciences). Yu.E. Gorbaty, A.B. Belonoshko, V.N. Balashov, K.I. Shmulovich, and I.V. Zakirov (same institute) took active part in discussions of our results. We thank A.G. Kalinichev (same institute) for continuous interest in our study and constructive criticism of the
manuscript. We are indebted to S.D. Malinin (Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences) for his benevolent review. The study was supported by the Russian Foundation for Basic Research, project no. 96-05-64396, and INTAS, grant no. 94-3138.

REFERENCES

Alunin, V.V., Teplofizicheskie svoistva dvukoi ugleroda (Thermal Properties of Carbon Dioxide), Moscow: Izd. Standartov, 1975.


Haar, L., Gallaher, J.C., and Kell, G.S., NBS/NRC Steam Tables: Thermodynamic and Transport Properties and Com-


