

## **Equations of State Valid Continuously from Zero to Extreme Pressures with H<sub>2</sub>O and CO<sub>2</sub> as Examples<sup>1</sup>**

**K. S. Pitzer<sup>2</sup> and S. M. Sterner<sup>2,3,4</sup>**

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A new form of equation of state is proposed for use over extremely wide ranges of pressure where conventional equations fail. In particular, fluids, including H<sub>2</sub>O and CO<sub>2</sub> as well as argon, etc., remain more compressible at very high densities than can be represented by typical equations with van der Waals or Carnahan and Starling repulsive terms. The new equation is fitted to the data for H<sub>2</sub>O and CO<sub>2</sub> over the entire range from the vapor and liquid below the critical temperature to at least 2000 K and from zero pressure to more than 10<sup>5</sup> bar (10 GPa) with good agreement. The extension of the equation for mixed fluids is discussed.

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**KEY WORDS:** carbon dioxide; fluid properties; high pressures; high temperatures; water.

### **1. INTRODUCTION**

Considerable information is now available concerning the properties of both simple fluids such as argon and other important fluids such as H<sub>2</sub>O and CO<sub>2</sub> at pressures extending to tens and even hundreds of kilobars. Particularly important are the shock-compression measurements of Nellis et al. [1] and of Schott [2] on CO<sub>2</sub> and of Walsh and Rice [3] and Lyzenga et al. [4] on H<sub>2</sub>O which yield information at high temperature for very high pressure. Also pertinent is information on diamond-anvil compression measurements at lower temperatures for CO<sub>2</sub> from Olinger [5] and Liu [6] and similar experiments on water.

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<sup>2</sup> Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, U.S.A.

<sup>3</sup> Bayerisches Geoinstitut, Universität Bayreuth, Postfach 101251, D-95440 Bayreuth, Germany.

<sup>4</sup> Author to whom correspondence should be addressed. Present address: Battelle Pacific Northwest Laboratories, Richland, Washington 99352, U.S.A.

Extrapolations of the low-pressure equations of state in current use into this range are not satisfactory. While various equations have been proposed that represent a particular set of high-pressure data, these are not valid at lower ranges of  $T$  and  $P$ . It would be desirable to incorporate the high-pressure information with that for lower pressures into a single equation of state for an extended range. For example, there are geological problems in the 10- 50-kbar (1-5 GPa) range which cannot be treated properly without such an equation for  $\text{CO}_2$ .

We now know that the repulsive interaction between molecules at short distances is not as steep as had long been thought or as is implied by many equations in current use. Thus, the interatomic potential for argon [7-12] is not well approximated at very short distances by an inverse-power potential, as was shown by measurements of atomic scattering and of the shock-compressed fluid. Accurate expressions for the interatomic potential of argon [7-12] are now available, but they are complex, and macroscopic properties have only been obtained by simulation methods. Many equations of state in current use have repulsive terms of the van der Waals or the Carnahan and Starling [13] type which yield infinite pressure at a finite volume. Such expressions are inappropriate for this domain of very high pressure. Other equations of state involve many terms in increasing powers of the density. With enough terms the measured properties can be represented, but such equations rarely yield meaningful extrapolations to higher densities. Rather, they predict either an unrealistically rapid increase in pressure toward infinity (if the term in the highest power of density has a positive coefficient) or a false maximum in pressure and subsequent decrease (if that term has a negative sign.)

Examination of the observed properties of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and other fluids in this range of very high pressure showed, however, a very simple behavior (Figs. 1-3). It is well represented by a simple expression dominated by a term linear in density for the compression factor  $z = P/\rho RT$  (or quadratic in density for the pressure). One option is to combine an expression for the high-density region with another equation for lower densities [14]. But this is inconvenient, and especially so when derivatives are needed in border regions between equations. Alternatively, simulations or other approximate calculations are based on intermolecular potentials, but for  $\text{CO}_2$  or  $\text{H}_2\text{O}$ , in contrast to Ar, the potentials used are grossly oversimplified and have only empirical validity [1, 14]. Such results are useful for the pressure or other function calculated, but cannot be differentiated or integrated easily to yield other thermodynamic quantities. In this paper we present a single complete equation of state which combines a simple expression for the high-density region with additional terms to represent

the more complex behavior at lower densities including the critical region and vapor-liquid phase separation.

As one proceeds from a pure to a mixed fluid, it is especially advantageous to have a relatively simple format for the equation and to use the same format for each pure fluid. Only then can appropriate expressions for mixing be introduced in a manner consistent with basic principles and without undue complexity [15, 16]. Applications to geologically important mineral equilibria involving  $\text{CO}_2$  are considered in a separate paper [17], which also discusses in greater detail the precision of fit of the new equation to experimental data. We emphasize here the selection of a novel format for the equation and demonstrate its capacity to represent data over the extremely wide ranges of  $T$  and  $P$ .

## 2. EQUATION

The equation of state is initially defined for the residual (nonideal) Helmholtz energy at a given temperature as

$$A^{\text{res}}/nRT = c_1\rho + [1/(c_2 + c_3\rho + c_4\rho^2 + c_5\rho^3 + c_6\rho^4) - 1/c_2] \\ - (c_7/c_8)[\exp(-c_8\rho) - 1] - (c_9/c_{10})[\exp(-c_{10}\rho) - 1] \quad (1)$$

Here,  $\rho$  is the density, and the first term on the right is the dominant term at high density. The second term provides the major effect at all intermediate densities, while the two exponential terms provide fine adjustments in the region of low and near-critical densities. For the pressure, the appropriate differentiation, after adding the ideal gas term, yields

$$P/RT = \rho + c_1\rho^2 - \rho^2 \left[ \frac{(c_3 + 2c_4\rho + 3c_5\rho^2 + 4c_6\rho^3)}{(c_2 + c_3\rho + c_4\rho^2 + c_5\rho^3 + c_6\rho^4)^2} \right] \\ + c_7\rho^2 \exp(-c_8\rho) + c_9\rho^2 \exp(-c_{10}\rho) \quad (2)$$

Expansion of various terms yields the virial coefficients; the second is

$$B = c_1 - c_3/c_2^2 + c_7 + c_9 \quad (3)$$

Each parameter  $c_1$  through  $c_{10}$  is, in principle, temperature dependent. We represent this by a simple polynomial

$$c_i = c_{i,1}T^{-4} + c_{i,2}T^{-2} + c_{i,3}T^{-1} + c_{i,4} + c_{i,5}T + c_{i,6}T^2 \quad (4)$$

In our calculations only two or three terms are usually required, with four terms the maximum and with only the constant term  $c_{6,4}$  for  $c_6$ . In order to obtain plausible extrapolations of properties to temperatures above the

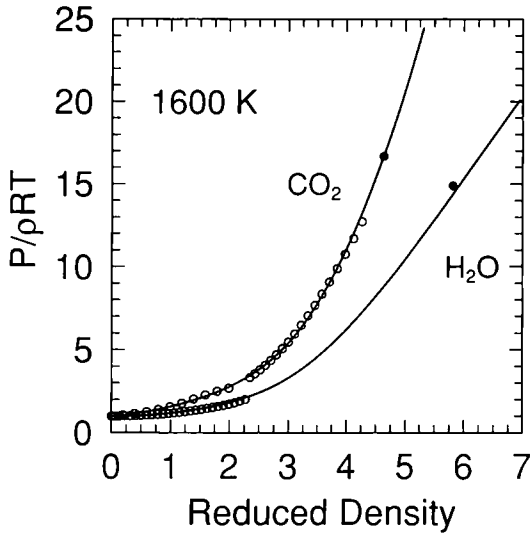


Fig. 1. The compression factor  $z = P/RT\rho$  for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  for 1600 K as a function of reduced density  $\rho_r = \rho/\rho_c$ . The curves are calculated and the solid circles show the values from shock-compression measurements. The open circles show other input data (see text).

range of accurate measurements, only negative powers of  $T$  were used for  $c_1$  and  $c_7-c_{10}$ , in addition to constant terms. For  $c_2-c_6$ , which are in the denominator in Eq. (1), terms with positive powers of  $T$  dominate at high temperatures.

### 3. EXPERIMENTAL DATA

The full arrays of data used for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are listed and discussed elsewhere [17, 18]. For the general region of  $T$  and  $P$ , well-established equations of state for  $\text{CO}_2$  [19-21]<sup>5</sup> and  $\text{H}_2\text{O}$  [23] are used as data bases for the present calculations. The second virial coefficient is extrapolated upward in  $T$  by corresponding-state comparisons [24] of  $\text{CO}_2$  with  $\text{N}_2$ , Ne, and He and then of  $\text{H}_2\text{O}$  with  $\text{CO}_2$ . For  $\text{CO}_2$  in the range of 2-8 kbar and for temperatures to 980 K, the data and equation of Shmonov and Shmulovich [25] were used.

Most important are the shock-compression measurements. For  $\text{CO}_2$ , values were interpolated from the curves of Nellis et al. [1], which include

<sup>5</sup> Also revised parameters from Ely [22].

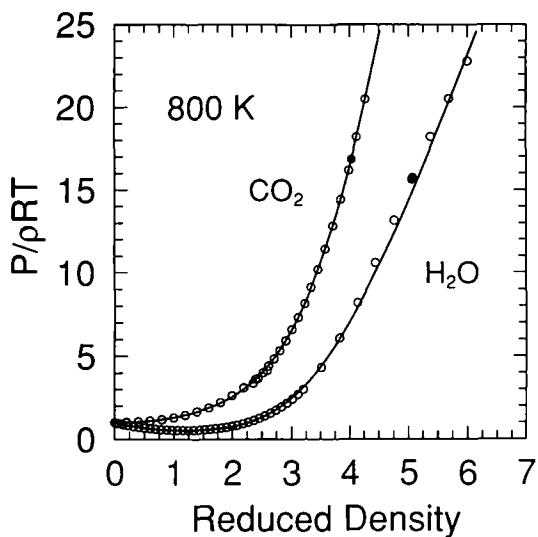


Fig. 2. The compression factor  $z = P/RT\rho$  for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  for 800 K as a function of reduced density  $\rho_r = \rho/\rho_c$ . The curves are calculated and the circles show experimental and other input data (see text).

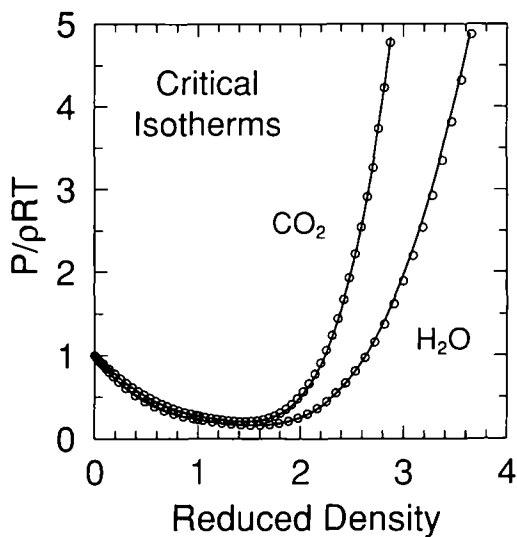


Fig. 3. The compression factor  $z = P/RT\rho$  for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at their respective critical temperatures, 304.13 and 647.14 K, as a function of reduced density  $\rho_r = \rho/\rho_c$ . Details as in Fig. 2.

Table I. Coefficients  $c_{i,j}$  of Eq. (4) for CO<sub>2</sub> and H<sub>2</sub>O

$i$	$c_{i,1}$	$c_{i,2}$	$c_{i,3}$	$c_{i,4}$	$c_{i,5}$	$c_{i,6}$
CO <sub>2</sub>						
1	***	***	+0.18261340E+7	+0.79224365E+2	***	***
2	***	***	***	+0.66560660E-4	+0.57152798E-5	+0.30222363E-9
3	***	***	***	+0.59957845E-2	+0.71669631E-4	+0.62416103E-8
4	***	***	-0.13270279E+1	-0.15210731E+0	+0.53654244E-3	-0.71115142E-7
5	***	***	+0.12456776E+0	+0.49045367E+1	+0.98220560E-2	+0.55962121E-5
6	***	***	***	+0.75522299E+0	***	***
7	-0.39344644E+12	+0.90918237E+8	+0.42776716E+6	-0.22347856E+2	***	***
8	***	***	+0.40282608E+3	+0.11971627E+3	***	***
9	***	+0.22995650E+8	-0.78971817E+5	-0.63376456E+2	***	***
10	***	***	+0.95029765E+5	+0.18038071E+2	***	***
H <sub>2</sub> O						
1	***	***	+0.24657688E+6	+0.51359951E+2	***	***
2	***	***	+0.58638965E+0	-0.28646939E-2	+0.31375577E-4	***
3	***	***	-0.62783840E+1	+0.14791599E-1	+0.35779579E-3	+0.15432925E-7
4	***	***	***	-0.42719875E+0	-0.16325155E-4	***
5	***	***	+0.56654978E+4	-0.16580167E+2	+0.76560762E-1	***
6	***	***	***	+0.10917883E+0	***	***
7	+0.38878656E+13	-0.13494878E+9	+0.30916564E+6	+0.75591105E+1	***	***
8	***	***	-0.65537898E+5	+0.18810675E+3	***	***
9	-0.14182435E+14	+0.18165390E+9	-0.19769068E+6	-0.23530318E+2	***	***
10	***	***	+0.92093375E+5	+0.12246777E+3	***	***

the results of Schott [2], for a series of values along the Hugoniot to 4000 K. These were augmented by some values calculated by the method of Ree [26] from the potential "A" of Nellis et al. [1]. For  $\text{H}_2\text{O}$ , there are measurements of Walsh and Rice [3] and Lyzenga et al. [4]; the latter extend to 5270 K and 800 kbar (80 GPa). Further details and comparisons with results from calculations based on empirical intermolecular potentials are discussed in Refs. 17 and 18.

#### 4. PARAMETER EVALUATION

The equation was fitted initially to the data for the critical temperature in each case, and for that calculation the requirement of zero values for the first and second density derivatives was introduced with substantial weight. After the parameters representing the critical isotherm had been determined, their temperature dependence was determined by fitting the data for other temperatures, including those for vapor-liquid equilibrium. In the region of very high  $P$  and  $T$  for both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , the shock compression values were given sufficiently high weights that the final equation agreed well within experimental uncertainty. In both cases, values of the second virial coefficient were included and related to Eq. (3). The equality of chemical potential between saturated vapor and liquid was introduced over the range 220–290 K for  $\text{CO}_2$  and 373–647 K for  $\text{H}_2\text{O}$ .

The parameters for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are given in Table I, while calculated curves are compared with input data in Figs. 1–3.

#### 5. DISCUSSION

Over the ranges of temperature and density where the experimental properties are accurately known, our equation yields agreement to about 1% and in many regions it has higher accuracy. The simple pressure-density pattern is very well established experimentally at 800 K (Fig. 2). But at higher temperatures, there is considerable uncertainty for the intermediate densities below that of the point on the Hugoniot.

It is a major advantage of a single equation extending over the full range of temperature and density that fugacities, enthalpies, entropies, and other related properties can all be calculated conveniently. In particular, the fugacity can be related directly to the residual Helmholtz energy. In a separate paper [17] the fugacity of  $\text{CO}_2$  is calculated and related to mineral equilibria which have been reported in the range extending to 1700 K and 50 kbar (5 MPa). This equation can be extended to mixed fluids by use of the same form of equation for each pure fluid. Theoretical factors related to mixtures are discussed in Ref. 18.

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