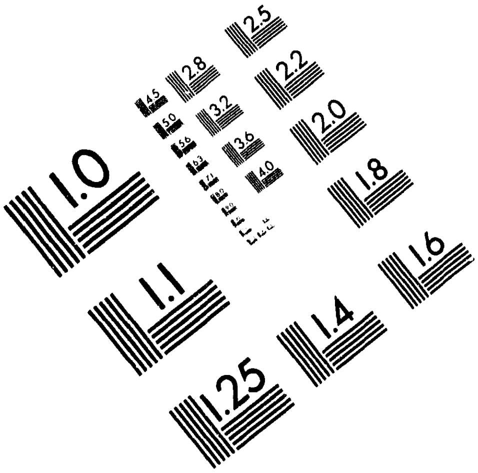

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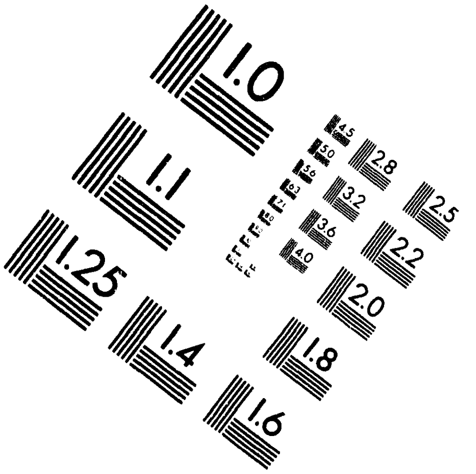

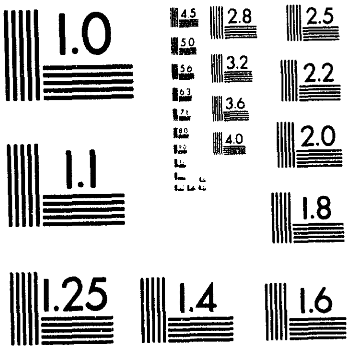

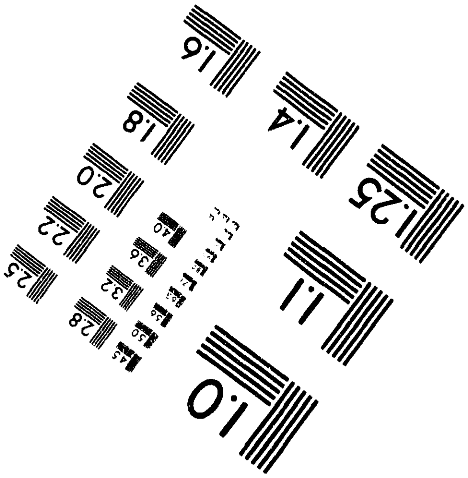

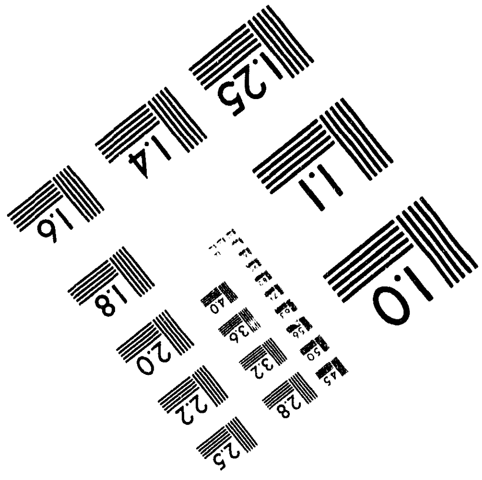

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Equations of State Valid Continuously from Zero to Extreme Pressures with H_2O and CO_2 as Examples

K.S. Pitzer and S.M. Sterner

March 1994

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Equations of State Valid Continuously from Zero to Extreme Pressures with H_2O and CO_2 as Examples

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19-24, 1994, Boulder, Colorado, U.S.A.

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ABSTRACT

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_2O and CO_2 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_2O and CO_2 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 10^5 bars (10 GPa) with good agreement. The extension of the equation for mixed fluids is discussed.

1. INTRODUCTION

Considerable information is now available concerning the properties of both simple fluids such as argon and other important fluids such as H_2O and CO_2 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_2 and of Walsh and Rice[3] and Lyzenga et al.[4] on H_2O which yield information at high temperature for very high pressure. Also pertinent is information on diamond-anvil compression measurements at lower temperatures for CO_2 from Olinger[5] and Liu[6] and similar experiments on water.

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 CO_2.

We now know that the repulsive interaction between molecules at short distances is not as sudden 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 clearly 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 H_2O, 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 CO_2 or H_2O, 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 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

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

Here, ρ 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

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

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

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

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

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

In our actual 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 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 CO_2 and H_2O are listed and discussed elsewhere.[17,18] For the central region of T and P, well established equations of state for CO_2[19-21] and H_2O[22] are used as data bases for the present calculations. The second virial coefficient is extrapolated upward in T by corresponding-state comparisons[23] of CO_2 with N_2, Ne, and He and then of H_2O with CO_2. For CO_2 in the range 2-8 kbar and for temperatures to 980 K the data and equation of

Shmonov and Shmulovich[24] was used.

Most important are the shock-compression measurements. For CO_2 values were interpolated from the curves of Nellis et al.[1], which include the results of Schott,[2] for a series of values along the Hugoniot to 4000 K. These were augmented by some values calculated for us a from model potential by Dr. F. H. Ree. For H_2O 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 references 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 for the critical temperature had been determined, their temperature dependency 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 CO_2 and H_2O, 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 K to 290 K for CO_2 and 373 to 647 K for H_2O.

The parameters for CO_2 and H_2O are given in Table I, while calculated curves are compared with input data on Figs. 1, 2, and 3.

4. DISCUSSION

Over the ranges of temperature and density where the experimental properties are accurately known, our equation yields agreement to about one percent and in many regions 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 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 reference 18.

ACKNOWLEDGMENTS

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Table I. Coefficients $c_{i,j}$ of Eq. (4) for CO_2 and H_2O

i	$c_{i,1}$	$c_{i,2}$	$c_{i,3}$	$c_{i,4}$	$c_{i,5}$	$c_{i,6}$
			CO_2			
1	* * *	* * *	$+.18261340E+7$	$+.79224365E+2$	* * *	* * *
2	* * *	* * *	* * *	$+.66560660E-4$	$+.57152798E-5$	$+.30222363E-9$
3	* * *	* * *	* * *	$+.59957845E-2$	$+.71669631E-4$	$+.62416103E-8$
4	* * *	* * *	$-.13270279E+1$	$-.15210731E+0$	$+.53654244E-3$	$-.71115142E-7$
5	* * *	* * *	$+.12456776E+0$	$+.49045367E+1$	$+.98220560E-2$	$+.55962121E-5$
6	* * *	* * *	* * *	$+.75522299E+0$	* * *	* * *
7	$-.39344644E+12$	$+.90918237E+8$	$+.42776716E+6$	$-.22347856E+2$	* * *	* * *
8	* * *	* * *	$+.40282608E+3$	$+.11971627E+3$	* * *	* * *
9	* * *	$+.22995650E+8$	$-.78971817E+5$	$-.63376456E+2$	* * *	* * *
10	* * *	* * *	$+.95029765E+5$	$+.18038071E+2$	* * *	* * *
			H_2O			
1	* * *	* * *	$+.24657688E+6$	$+.51359951E+2$	* * *	* * *
2	* * *	* * *	$+.58638965E+0$	$-.28646939E-2$	$+.31375577E-4$	* * *
3	* * *	* * *	$-.62783840E+1$	$+.14791599E-1$	$+.35779579E-3$	$+.15432925E-7$
4	* * *	* * *	* * *	$-.42719875E+0$	$-.16325155E-4$	* * *
5	* * *	* * *	$+.56654978E+4$	$-.16580167E+2$	$+.76560762E-1$	* * *
6	* * *	* * *	* * *	$+.10917883E+0$	* * *	* * *
7	$+.38878656E+13$	$-.13494878E+9$	$+.30916654E+6$	$+.75591105E+1$	* * *	* * *
8	* * *	* * *	$-.65537898E+5$	$+.18810675E+3$	* * *	* * *
9	$-.14182435E+14$	$+.18165390E+9$	$-.19769068E+6$	$-.23530318E+2$	* * *	* * *
10	* * *	* * *	$+.92093375E+5$	$+.12246777E+3$	* * *	* * *

FIGURE CAPTIONS

Fig. 1. The compression factor $z = P/RT\rho$ for CO_2 and H_2O 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).

Fig. 2. The compression factor $z = P/RT\rho$ for CO_2 and H_2O 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 CO_2 and H_2O at their respective critical temperatures, 304.13 K and 647.14 K as a function of reduced density $\rho_r = \rho/\rho_c$. Details as in Fig. 2.

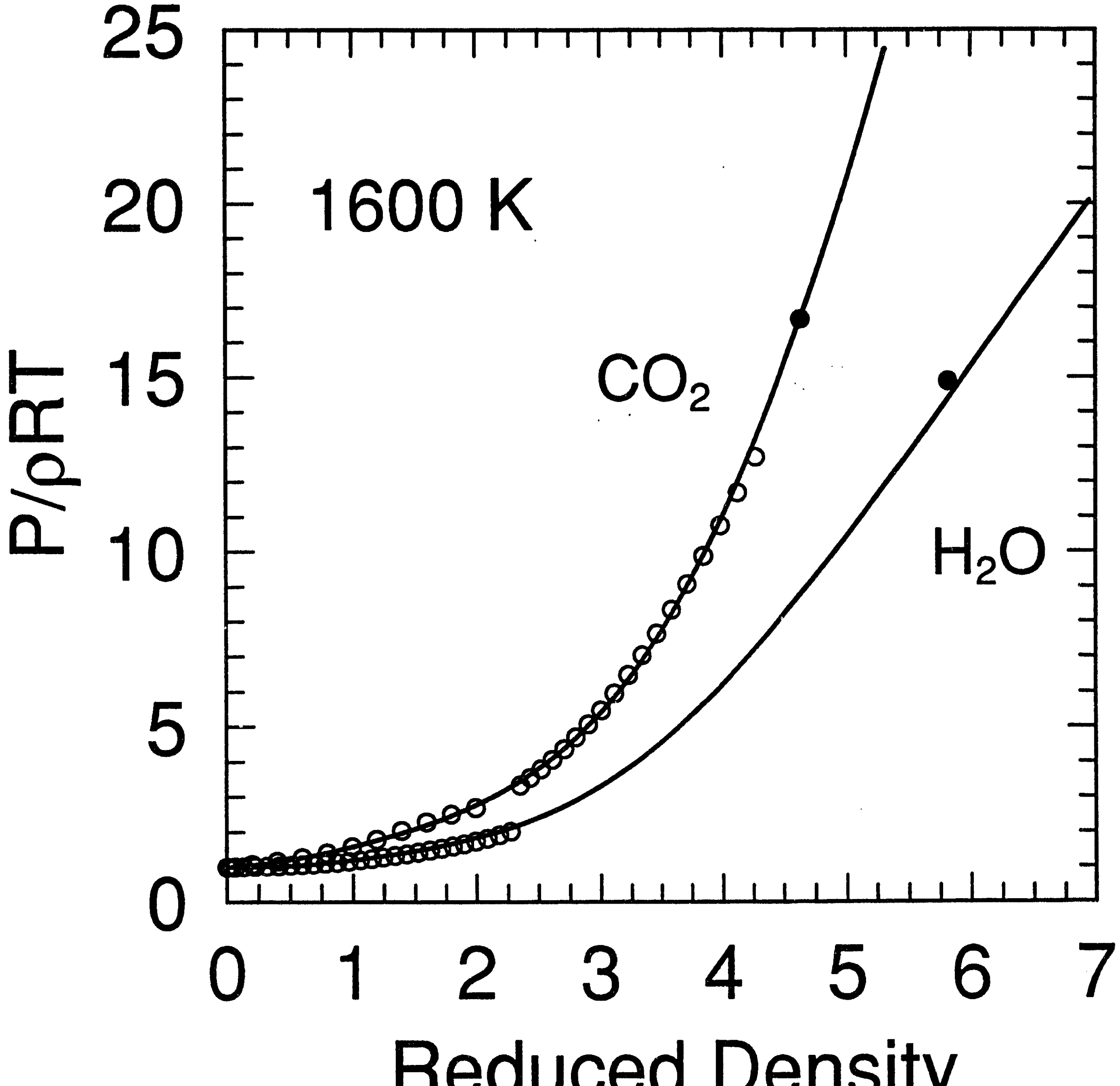

Fig. 1

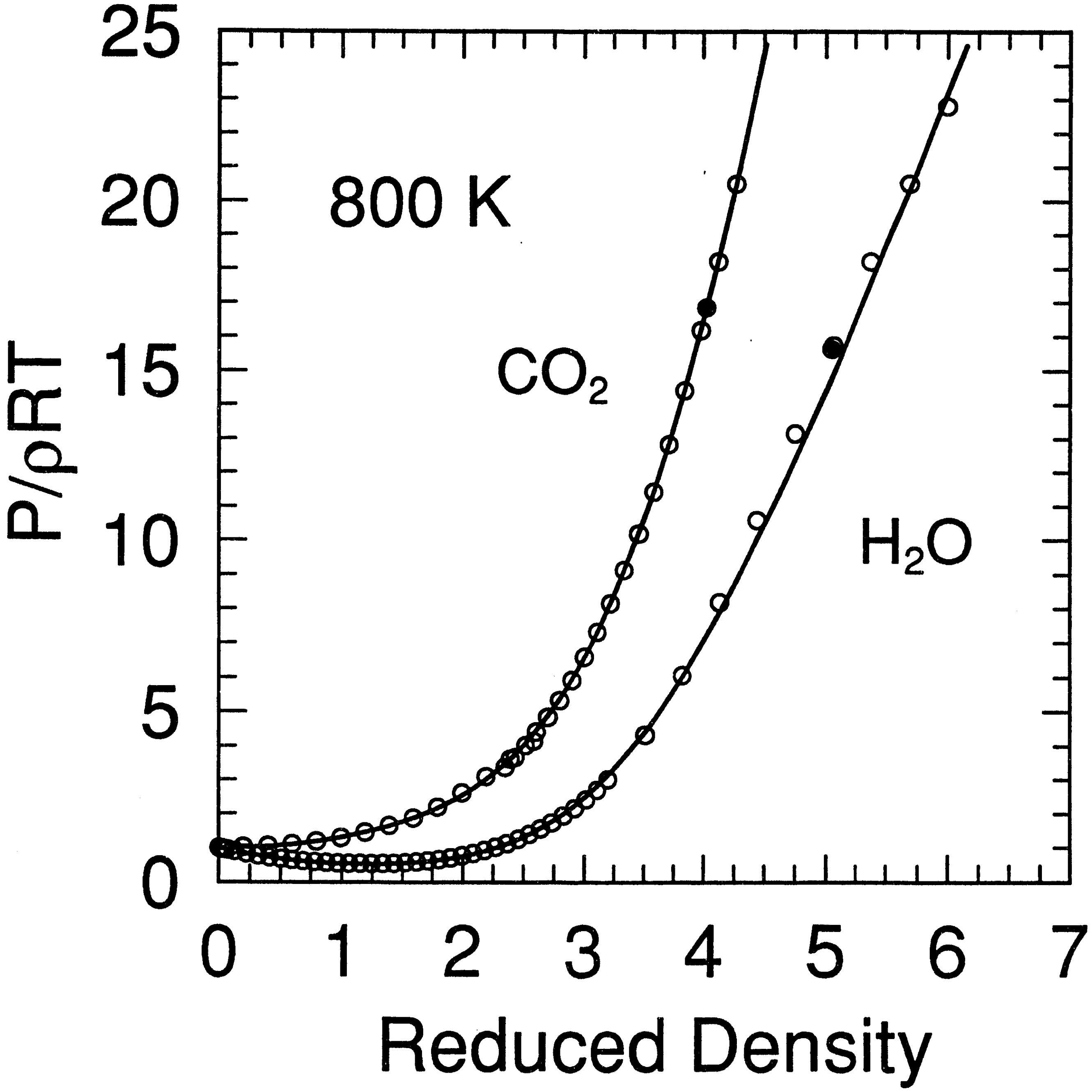

Fig. 2

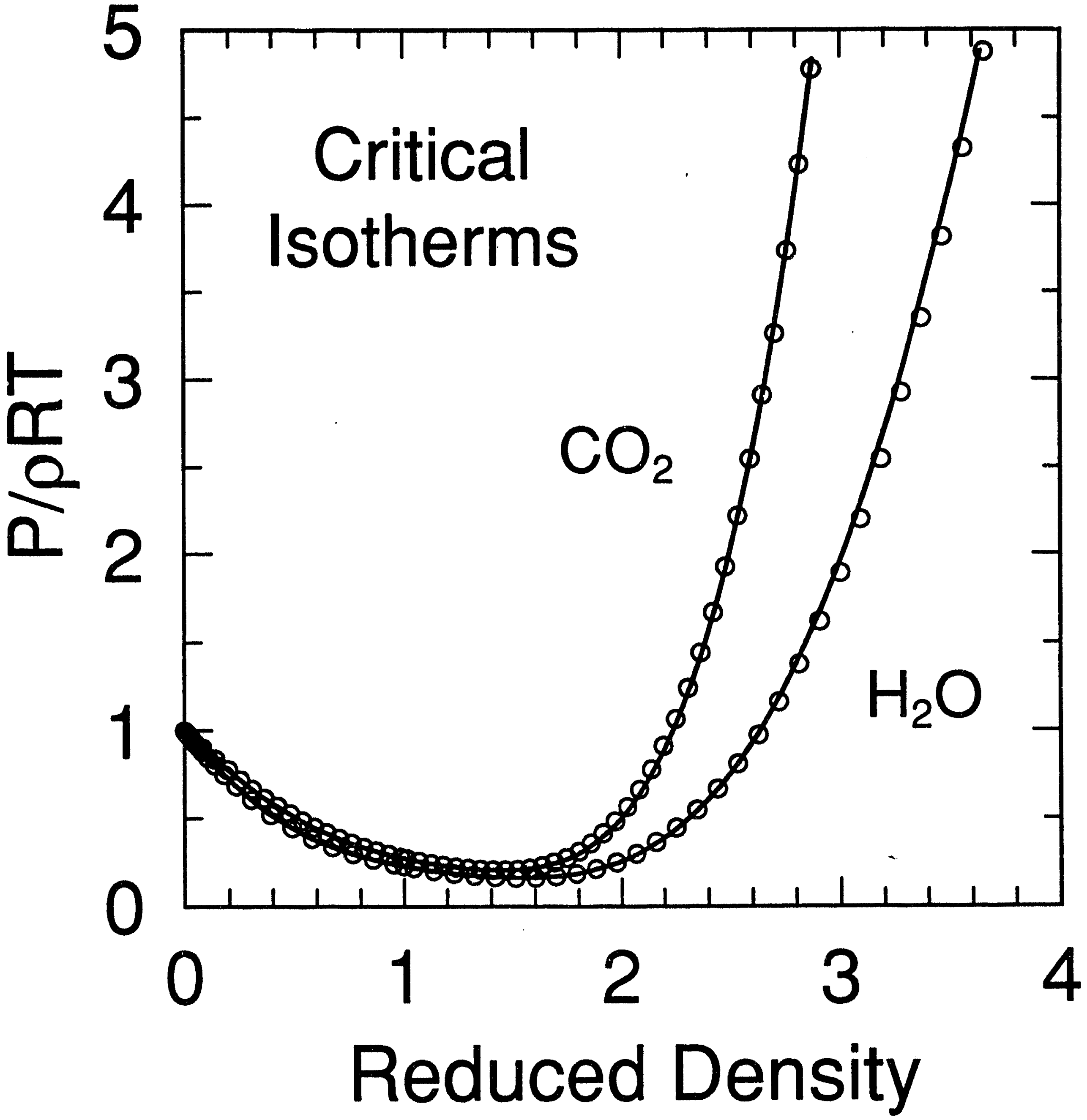
Critical
Isotherms
CO_2
H_2O
P/ρRT
0
1
2
3
4
5
Reduced Density
0
1
2
3
4

Fig. 3

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