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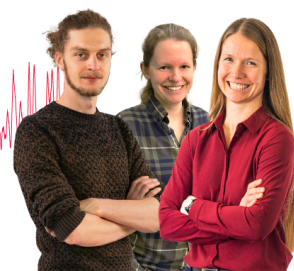
Equations of state valid continuously from zero to extreme pressures for H_2O and CO_2

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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_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 bar (10 GPa) with good agreement. The extension of the equation for mixed fluids is discussed.

I. 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 den-

sity. 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, 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, 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 equa-
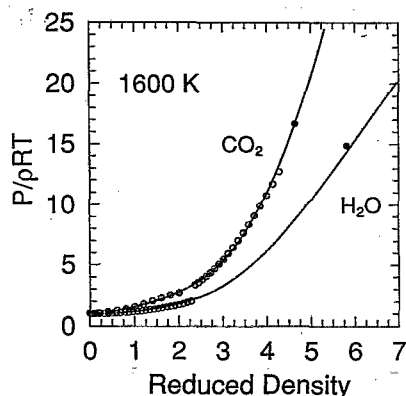
FIG. 1. The compression factor $z = P/RT\rho$ for CO_2 and H_2O for 1600 K as a function of reduced density $\rho_r = \rho/\rho_c$. The curves are calculated and the solid circles show the values from shock-compression measurements. The open circles show other input data (see the text).

tion and demonstrate its capacity to represent data over the extremely wide ranges of T and P.

II. EQUATION

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

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

Here, $\rho = n/V$ is the density in mol cm^{-3}, 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
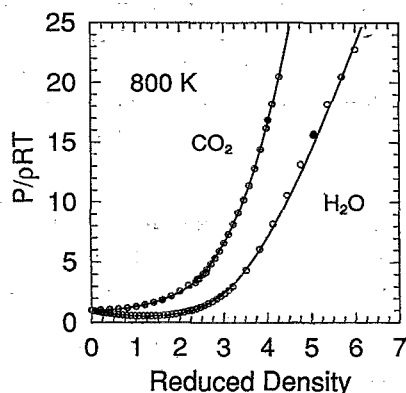

FIG. 2. The compression factor $z = P/RT\rho$ for CO_2 and H_2O for 800 K as a function of reduced density $\rho_r = \rho/\rho_c$. The curves are calculated and the circles show experimental and other input data (see the text).
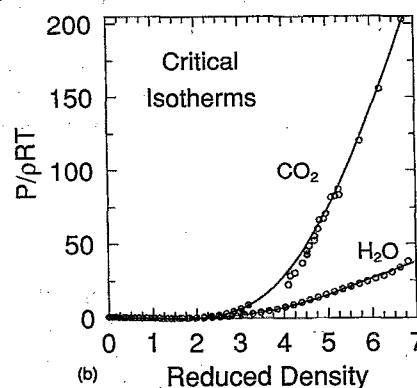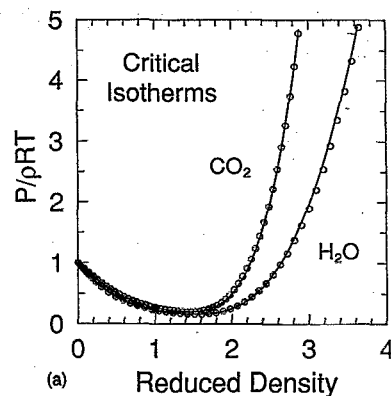

FIG. 3. (a) The compression factor $z = P/RT\rho$ for CO_2 and H_2O at their respective critical temperatures 304.13 and 647.14 K as a function of reduced density $\rho_r = \rho/\rho_c$ for two ranges of ρ_r and z. Details are the same as in Fig. 2.

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

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

$$B = c_1 - c_3/c_2^2 + c_7 + c_9. \tag{3}$$

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

$$c_i = c_{i,1}T^{-4} + c_{i,2}T^{-2} + c_{i,3}T^{-1} + c_{i,4} + c_{i,5}T + c_{i,6}T^2. \tag{4}$$

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.

III. EXPERIMENTAL DATA

For carbon dioxide in the region of moderate pressure and temperature, there seemed to be no need to reevaluate the extensive array of thermodynamically interrelated data. The recent investigation of CO_2 by Ely et al.[18] considered such data including that of the recent paper of Holste et al.[19] We accepted the properties given by the Ely et al. equation over the range from 220 to 330 K and up to 300 bar. For the broader range to 1100 K and 2 kbar, we adopted the properties given by the equation of Altunin and Gadetskii[20] which was adopted in the IUPAC study of Angus et al.[21] These two equations are in good agreement in the region of common validity, although there is every reason to use the more recent equation of Ely et al.,[18] where it is applicable. Values of the second virial coefficient from Altunin and Gadetskii[20] were extended upward in temperature by corresponding-states comparisons with N_2 to 1600 K and with Ne and He to temperatures above 2000 K using data from Dymond and Smith.[22] These comparisons were referenced to the Boyle point rather than the critical point; at these high reduced temperatures, there is little departure from corresponding states behavior. The estimate for 2000 K was 30.2 cm^3 mol^{-1}.

At pressures from 2 to 7 kbar and temperatures to 673 K, there are volumetric data from Tsiklis et al.,[23] while from 2 to 8 kbar and higher temperatures to 980 K, there are similar measurements of Shmonov and Shmulovich.[24] The latter authors present an equation representing their own and other data from 2 to 8 kbar over the full temperature range of measurement. Since the temperature dependency is very simple, this equation was assumed to be valid for temperatures below that of the lowest temperature of measurement, even into the range of supercooled liquid.

The primary source of information for still higher pressures at high temperatures is that from shock-compression measurements. 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 by Dr. F. H. Ree from his model potential which fits both the shock compression data[1] and the static measurements of Shmonov and Shmulovich.[24] Specifically, this was an "exponential-six" potential (see Ree[25]) with the parameters of set A of Nellis et al.[1] (ϵ/k=245.6 K, r^*=4.20 Å, and α=13.5). The values included in our data base were for the range 800–2000 K and densities 1.1–2.0 g cm^{-3}.

At low temperatures and high pressures, there are diamond–anvil compression data for solid CO_2 from Olinger[5] and Liu[6] which extend to 500 kbar at about 300 K; these are shown on Fig. 3(b). We assume that the pressure for the liquid exceeds that of the solid at the same density, but only by a small amount, and that this difference remains small in the range of very high total pressure. A very recent paper of Aoki et al.[26] appeared after our calculations were completed; it indicates slightly but not significantly higher pressures in the range near 120 kbar.

For H_2O, there is the recent and excellent 58-coefficient equation of Saul and Wagner[27] which represents quite satisfactorily volumetric and other data up to 1273 K and 10 kbar

and is reasonably concordant with the shock compression data of Mitchell and Nellis[28] at still higher temperature and pressure. We saw no need to reexamine the extensive data base used by Saul and Wagner,[27] nor did we seek data at higher pressures and low temperatures. Values calculated from their equation are shown in Figs. 1–3 and form our primary data base. There is another comprehensive equation of Hill[29] for H_2O. He gave greater emphasis to other P–T ranges and less to that at very high P; hence, his equation is less useful for our purposes.

The second virial coefficient for H_2O above 1200 K was estimated on a corresponding states basis from the data for CO_2. In this case, the reference must be to the critical point since experimental data for H_2O do not extend to its Boyle point, but in the range of reduced temperatures from 1.5 to 2.0, CO_2 and H_2O follow corresponding states closely for the second virial coefficient. Thus, this extrapolation for H_2O to higher temperatures should be satisfactory.

In addition to values calculated from the equation of Saul and Wagner,[27] and the extrapolated values of the second virial coefficient, we included high-density values based on the shock compression measurements of Walsh and Rice[3] as interpreted by Rice and Walsh.[30] These are shown as solid circles on Figs. 1 and 2. For still higher P and T, there are similar measurements of Lyzenga et al.[4] which extend to 5270 K and 800 kbar. For temperatures above 1200 K and intermediate densities below that of the Hugoniot but above the range where the second virial coefficient is dominant, there are no experimental values. We included values from Saul and Wagner's equation, but gave them low weight. We also compared with values of Belonoshko and Saxena,[14] which are based on an empirical "exponential-six" potential. Our final equation yields values intermediate between those of Saul and Wagner and those of Belonoshko and Saxena in this range, and presents, we believe, the best estimates available at this time.

IV. PARAMETER EVALUATION

In addition to an extensive array of P–V–T and Helmholtz energy values from sources described above, the database for parameter evaluation included other types of data. 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 CO_2 and 373–647 K for H_2O.

The equation was fitted initially to the data for the critical temperature in each case, and for that calculation, the requirement of zero values at T_c, ρ_c for the first and second density derivatives was introduced with substantial weight. At the critical temperature, CO_2 is solid at pressures above about 6 kbar. Extrapolated values from the equation of Shmonov and Shmulovich[24] were included for the supercooled liquid to 8 kbar. For higher pressures and densities at T_c, we assumed that the supercooled liquid would approach the solid in density at extremely high pressures. Thus, we made comparisons with values from the diamond–anvil pressure-cell measurements of Liu.[6] Our equation yields

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	...	...	+0.182 613 40E+7	+0.792 243 65E+2	...	...
2	...	...	...	+0.665 606 60E-4	+0.571 527 98E-5	+0.302 223 63E-9
3	...	...	...	+0.599 578 45E-2	+0.716 696 31E-4	+0.624 161 03E-8
4	...	...	-0.132 702 79E+1	-0.152 107 31E+0	+0.536 542 44E-3	-0.711 151 42E-7
5	...	...	+0.124 567 76E+0	+0.490 453 67E+1	+0.982 205 60E-2	+0.559 621 21E-5
6	...	...	...	+0.755 222 99E+0	...	...
7	-0.393 446 44E+12	+0.909 182 37E+8	+0.427 767 16E+6	-0.223 478 56E+2	...	...
8	...	...	+0.402 826 08E+3	+0.119 716 27E+3	...	...
9	...	+0.229 956 50E+8	-0.789 718 17E+5	-0.633 764 56E+2	...	...
10	...	...	+0.950 297 65E+5	+0.180 380 71E+2	...	...
			H_2O			
1	...	...	+0.246 576 88E+6	+0.513 599 51E+2	...	...
2	...	...	+0.586 389 65E+0	-0.286 469 39E-2	+0.313 755 77E-4	...
3	...	...	-0.627 838 40E+1	+0.147 915 99E-1	+0.357 795 79E-3	+0.154 329 25E-7
4	...	...	...	-0.427 198 75E+0	-0.163 251 55E-4	...
5	...	...	+0.566 549 78E+4	-0.165 801 67E+2	+0.765 607 62E-1	...
6	...	...	...	+0.109 178 83E+0	...	...
7	+0.388 786 56E+13	-0.134 948 78E+9	+0.309 165 64E+6	+0.755 911 05E+1	...	...
8	...	...	-0.655 378 98E+5	+0.188 106 75E+3	...	...
9	-0.141 824 35E+14	+0.181 653 90E+9	-0.197 690 68E+6	-0.235 303 18E+2	...	...
10	...	...	+0.920 933 75E+5	+0.122 467 77E+3	...	...

higher pressures for the liquid than the solid at intermediate densities, but this difference decreases to near zero at 200 kbar.

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.

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.

A. A corresponding states comparison for H_2O and CO_2

The behavior of most neutral-molecule, nonmetallic fluids when compared on a corresponding state basis is well known. Departures are significant, but moderate and are well represented by the acentric factor system for molecules of low polarity. Water and carbon dioxide depart from corresponding states substantially, even at critical density and temperature with $z_c = P_c/\rho_c RT_c$ of 0.274 for CO_2 and 0.229 for H_2O. And from Figs. 3 and 4, the difference rapidly becomes much greater above a reduced density of 2. Since H_2O and CO_2 follow corresponding states for their second virial coefficients rather closely for reduced temperatures above 1.5, their reduced two-body potentials must be similar when spherically averaged for a high reduced temperature. The interaction potentials for three or more molecules, however, must differ significantly and be the primary source of the difference in z near critical density. This is reasonable in view of their very different types of attractive interactions. As the reduced density increases above 3, the molecules

pushed up their multibody intermolecular repulsive potentials by the high external pressure. And here it is apparent that H_2O and CO_2 are very different. The CO_2 molecule is much less compressible, or in other words, the repulsive branch of its intermolecular potential is much steeper than that of H_2O. While these concepts could be expressed quantitatively in intermolecular potential functions, that is beyond the scope of this paper.

V. MIXED FLUIDS

While no numerical calculations for a mixed system will be presented here, there is great geological interest in the CO_2–H_2O mixed fluid at very high temperatures and pressures. Thus, it is interesting to consider certain features of this new equation when extended to a mixture. Equations (1)
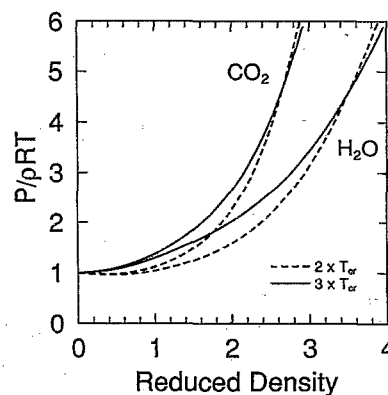

FIG. 4. The compression factor $z = P/RT\rho$ for CO_2 and H_2O on a corresponding states basis at $T_r = 2.0$ (dashed lines) and $T_r = 3.0$ (solid lines).

and (2) can represent such a fluid, but now the parameters $c_1 - c_{10}$ become functions of composition as well as temperature. There are principles from statistical mechanics that limit the composition dependency of each virial coefficient.[15,16]

The second virial coefficient arises from binary collisions or interactions. Thus for an $\alpha + \beta$ system, only $\alpha - \alpha$, $\alpha - \beta$, and $\beta - \beta$ effects are present and the expression for composition dependency of the second virial coefficient is

$$B = x_\alpha^2 B^{\alpha\alpha} + 2x_\alpha x_\beta B^{\alpha\beta} + x_\beta^2 B^{\beta\beta}. \tag{5}$$

If all of the parameters appearing in Eq. (3) were determined in the low-density range where the second virial coefficient dominates, Eq. (5) could be applied in a straightforward manner to each term. Actually, c_1 is determined primarily by the high-density range. Interactions of many molecules are involved, and there are no theoretical limits on the possible composition dependency of c_1. The moderately high density data that are available for $CO_2 - H_2O$ indicate a composition dependency that is rather simple, but more complex than quadratic.

While the requirement of Eq. (5) can only apply rigorously to the sum of terms in Eq. (3), it seems reasonable to apply it separately to the sum of the first two terms and to c_7 and c_9. The latter terms are important only in the low density region. Then any composition dependency more complex than quadratic in c_1 must be canceled by the term c_3/c_2^2. This can be accomplished with a linear dependency of c_2 and the same dependency for c_3 as for c_1.

The parameters c_8 and c_{10} can, like c_2, be assigned linear dependency

$$c_j = x_\alpha c_j^\alpha + x_\beta c_j^\beta. \tag{6}$$

Then no new parameters arise for mixtures for c_2, c_8, and c_{10}. While the theoretical limits are relatively relaxed for c_4, c_5, and c_6, it seems likely that their composition dependency will not be more complex than that for c_1 and c_3, and a simpler dependency may suffice in some cases. Methods are available[16] for estimating composition dependencies of terms for equations of state of mixed fluids.

VI. 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. Near the critical point, there are deviations of one sign at subcritical density and the opposite sign at supercritical density. These are the inherent deviations of any mathematically analytic equation from the true limiting behavior represented by the Ising critical exponents. The simple, pressure-density pattern is very well established experimentally at 800 K (Fig. 2). The established range of the equation of Saul and Wagner[27] for H_2O extends only to 1273 K; hence, there is considerable uncertainty at higher temperatures for the intermediate densities below that of the point on the Hugoniot. As noted above, our curves for temperatures from 1400 to 2000 K lie between the extrapolated values of the Saul and Wagner equation and the Monte Carlo

simulations of Belonoshko and Saxena,[14] which are based on an empirical "exponential-six" potential. The calculated values for CO_2 in this range, which were described above, are fitted very satisfactorily as shown on Fig. 1. In Fig. 3, the deviant points at intermediate densities are for solid CO_2, and it is expected that the curve for the superpressured liquid would lie above.

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 calculation of the fugacity requires an integral of $z - 1$ over the full range from zero to the final density; thus, an equation valid over the full range is advantageous. 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).

Note added in proof. Experimental PVT data have just been published for H_2O for the range 1200 K to 1900 K at intermediate density [J. P. Brodholt and B. J. Wood, Geochim. Cosmochim. Acta **58**, 2143 (1994)]. As noted above, there had been no reliable information for this range and the equation is essentially an interpolation between the second virial coefficient and the shock compression data for high density. Comparison with the new results shows good agreement throughout, probably within experimental uncertainty, and confirms the equation in that range.

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