A SEMI-EMPIRICAL EXCESS PRESSURE EQUATION FOR 
\textit{CO}_2-\textit{H}_2\textit{O} FLUIDS AT 400\textdegree{C}, 0-400 MPa 

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ABSTRACT: Highly accurate and precise density data for \textit{CO}_2-\textit{H}_2\textit{O} mixtures at 400\textdegree{C}, 10-400 MPa, 
were used to develop a modified, B-truncated virial equation for excess pressure \((P^{ex})\). This function 
and empirical equations of state for \textit{H}_2\textit{O} and \textit{CO}_2 accurately represent the experimentally determined 
densities, and interpolate smoothly between data points. Integrating the \(P^{ex}\) expression with respect to 
molar volume yields an equation for excess Helmholtz free energy, which can be used to calculate other 
excess properties of interest. The \(P^{ex}\) modeling method has important advantages over more 
conventional, alternative approaches.

INTRODUCTION 
Mixed-volatile fluids are important in a wide variety of scientific disciplines and commercial 
activities [1-5]. Consequently, numerous equations of state (EOSs) have been developed to 
represent experimentally measured thermophysical properties for these mixtures, and to 
predict values for conditions unexplored by experimentation [4-7]. The latter need has 
prompted intense interest in theoretically based (semi-empirical) formulations [6-7], because 
they often interpolate and extrapolate more reliably than purely empirical expressions.

However, many widely applied semi-empirical EOSs—and particularly cubic expressions [8]—have three serious disadvantages: (1) their forms are too simple to accurately represent 
volumetric properties at pressure-temperature-composition (\(P-T-X\)) conditions near the 
critical point of a pure fluid; (2) to permit the use of mixing rules, the EOSs for all pure fluids 
must be of identical form; and (3) inaccuracies in calculated volumetric properties for pure 
fluids propagate to calculated excess properties for mixtures.

This paper presents a new semi-empirical EOS for binary, mixed-volatile fluids. It is explicit 
in excess pressure, applicable over wide ranges of temperature and pressure, and can 
accurately represent the excess volumetric properties of binary fluid mixtures at \(P-T-X\) 
conditions close to the critical point of a pure fluid. The latter capability is demonstrated by 
using it to model density data for \textit{CO}_2-\textit{H}_2\textit{O} mixtures at 400\textdegree{C}, 10-400 MPa.

A MODIFIED, B-TRUNCATED VIRIAL (MBV) MODEL 

With suitable EOSs (semi-empirical or empirical) for endmember (pure) volatile species, the 
excess volumetric properties of mixed-volatile fluids can be represented by an excess 
pressure \((P^{ex})\) -explicit function. \(P^{ex}\) is defined by the relation 

\[
P^{ex} = P - P^{id}, \tag{1}
\]

where \(P\) and \(P^{id}\) are, respectively, the pressure and ideal pressure of a fluid mixture of 
known composition. For a binary system:
\[ P^{\text{id}} = X_1 P_1^* + X_2 P_2^*. \] (2)

\[ P_1^* \text{ and } P_2^* \text{ are the pressures at which pure fluids 1 and 2 have the same molar volume (V) as the mixture.} \]

We have tested numerous \( P^{\text{id}} \)-explicit functions for binary, mixed-volatile fluids, and have determined that a theoretically based expression with empirical adjustable parameters can accurately represent excess volumetric properties from 0 MPa to elevated pressures where fluid behavior is partly to almost entirely "liquid-like." From 0 MPa to pressures where liquid-like behavior is first manifested, reliable values of \( P^{\text{id}} \) are obtained from the virial expression

\[ P^{\text{id}} = X_1 X_2 \left( \frac{RT(2B_{12} - B_{11} - B_{22})}{V^2} \right), \] (3)

which is derived from the \( P \)-explicit form of the B-truncated virial EOS,

\[ P = \frac{RT}{V} \left( 1 + \frac{B}{V} \right), \] (4)

with the mixing rule

\[ B = X_1^2 B_{11} + X_2^2 B_{22} + 2X_1 X_2 B_{12}. \] (5)

Equation 3 predicts that \( P^{\text{id}} \) vs. \( X \) is symmetric for all \( V \). However, for pressures high enough to induce a significant degree of liquid-like behavior, additional terms are needed to accurately correlate \( P^{\text{id}}(T,V,X) \) relations that are generally slightly to moderately asymmetric with respect to mole fraction, and which vary with \( V \) in a manner not reliably predicted by Equation 3.

A modified B-truncated virial (MBV) EOS with a mathematical form sufficiently flexible to accurately represent the excess volumetric properties of many binary, mixed-volatile fluids from 0 MPa to high pressures is:

\[ P^{\text{id}} = X_1 X_2 \left( \frac{RT(2B_{12} - B_{11} - B_{22})}{V^2} + X_1 W_{P,1} + X_2 W_{P,2} \right), \] (6)

where

\[ W_{P,1} = a_1 e^{a_1 V} + a_2 e^{a_2 V} + a_3 e^{a_3 V}, \]

\[ W_{P,2} = a_4 e^{a_4 V} + a_5 e^{a_5 V} + a_6 e^{a_6 V}, \]

and \( a_1-a_{12} \) are temperature-dependent regression coefficients. The first term in this expression is taken from Equation 3; the second and third terms permit accurate correlation of volumetric data for high pressures. Practical applications of the model require predetermined values for \( B_{11} \) and \( B_{22} \). An independently determined value for \( B_{12} \) may also be used, or calculated in the least-squares regression performed to quantify \( a_1-a_{12} \).
AN MBV FUNCTION FOR THE CO$_2$-H$_2$O SYSTEM AT 400°C, 0-400 MPa

Highly precise and accurate density data [9-12] were used to develop an MBV function (Equation 6) for CO$_2$-H$_2$O fluids at 400°C, 0-400 MPa. $B_{11}$ (B$_{H_2O-H_2O}$) = -72.6 ± 1.0 cm$^3$mol$^{-1}$ and $B_{22}$ (B$_{CO_2-CO_2}$) = -3.7 ± 1.0 cm$^3$mol$^{-1}$ were obtained from the literature [13-14]. Excess pressures were calculated from the density data using molar volumes for H$_2$O and CO$_2$ provided by empirical EOSs [15-16]. $B_{12}$ (B$_{H_2O-CO_2}$) and the empirical parameters in Equation 6 were quantified in the least-squares regression performed to correlate the excess pressures. The calculated value for $B_{H_2O-CO_2}$ = -16.2 ± 1.9 cm$^3$mol$^{-1}$ is in excellent agreement with the value given by the correlation of Vanderzee and Haas [17] (B$_{H_2O-CO_2}$ = -19.6 ± 7.0 cm$^3$mol$^{-1}$).

Excess molar volumes ($V^e$) for CO$_2$-H$_2$O fluids at 400°C, 9.94-99.93 MPa and 200-400 MPa, calculated from the $P^e$ model and the empirical EOSs for H$_2$O [15] and CO$_2$ [16], are illustrated in Figures 1 and 2, where they can be compared with excess molar volumes derived from the density data [9-12] and the same EOSs for H$_2$O and CO$_2$ that were used to calculate excess pressures. It can be seen that the MBV model represents the $V^e$ data accurately at all pressures except 19.94 MPa (Fig. 1a). For this pressure, calculated excess molar volumes are systematically slightly lower than experimentally determined values. If these discrepancies result entirely from fitting error, then it must be concluded that the mathematical form of Equation 6 is insufficiently flexible to precisely reproduce the excess volumetric properties of CO$_2$-H$_2$O mixtures at 400°C, 15-30 MPa. The opposite case—that the discrepancies are due entirely to experimental error—would be a more favorable result from a modeling standpoint, because it would suggest that Equation 6 has all the mathematical flexibility required to fit the excess volumetric properties of CO$_2$-H$_2$O mixtures at 400°C, and its use for that purpose can reveal small, systematic inaccuracies in experimentally determined excess molar volumes that are not readily detected by other means. The latter possibility is further indicated by the excess molar volumes for 400°C, 200-400 MPa, calculated from Equation 6 (Fig. 2). The sigmoidal trends of $V^e$ vs. composition for H$_2$O-rich fluids are irrational, and are plausibly ascribed to small, systematic error in the experimentally determined densities for these P-T conditions [12].

ADVANTAGES OF THE NEW EOS

The MBV EOS has numerous advantages over alternative semi-empirical models for binary mixed-volatile fluids. Because it is explicit in $P^e$ rather than $P$, it is used exclusively to represent the excess volumetric properties of binary fluid mixtures. The properties of the two pure-component fluids are represented by separate and completely independent EOSs, which may be semi-empirical or empirical, and of any suitable mathematical form. Used together, the set of equations behaves as a single EOS. This "modular" approach to EOS development circumvents many of the problems encountered in modeling the behavior of strongly nonideal, binary volatile fluids using a single, semi-empirical, $P$-explicit EOS.

Another important advantage of the MBV EOS is that it can accurately represent and predict the excess volumetric properties of binary mixed-volatile fluids over wide ranges of temperature and pressure. It's first term, derived from basic virial theory, provides reliable
excess volumetric properties for low-density mixtures, and ensures correct limiting thermodynamic behavior as \( P \to 0 \). The second and third terms ensure accurate representation of excess volumetric properties at high pressures; in effect, they correct the inaccurate excess pressures for “high-density” fluids given by the virial term. Specifically, the virial term predicts that, with increasing pressure (decreasing molar volume), \( P^\text{ex}(V) \) varies slowly and monotonically, and remains symmetric with respect to \( X \). However, our modeling calculations indicate that, as pressure rises above a certain threshold value, excess pressures begin to decrease sharply, and \( P^\text{ex}(V) \) vs. \( X \) becomes asymmetric. To account for these variations, the \( W_{p,1} \) and \( W_{p,2} \) parameters in the MBV EOS must be unequal, continuously negative, and must decrease exponentially with decreasing molar volume. This behavior is readily produced mathematically by series of exponential terms of the form \( a_i e^{a_i V} (i = 1, \ldots, j) \) (Equation 6), which also ensure that \( W_{p,1} \to 0 \) and \( W_{p,2} \to 0 \) as \( V \to \infty \) (\( P \to 0 \)). Negligibly small values for \( W_{p,1} \) and \( W_{p,2} \) at high molar volumes are required to allow the virial term to become predominant in predicting \( P^\text{ex} \) for low-density fluids.

Finally, Equation 6 can be integrated analytically to develop an expression explicit in excess Helmholtz free energy. This equation, in turn, can be used to compute other thermodynamic mixing properties of interest (excess Gibbs free energies, activity-composition relations, etc.).

**FUTURE WORK**

We plan to test Equation 6 more extensively in future modeling studies. An immediate goal is to use it to calculate densities, excess molar volumes and activity-composition relations for CO_2-H_2O mixtures at 400°C, 0-400 MPa, for comparison with results obtained from modified Redlich-Kwong and Lee-Kesler EOSs [6-7]. (Cross coefficients for terms in the latter models can be independently estimated, or derived by least-squares fitting to density data. Both approaches will be applied to determine their effects on the accuracy of calculated thermophysical properties.) It would also be instructive to use Equation 6 to correlate data for N_2-H_2O fluids at 400°C [18], because these mixtures have \( P-V-T-X \) properties similar to those of CO_2-H_2O fluids at that temperature. If the results of the foregoing studies indicate that further testing of Equation 6 is warranted, the next logical step would be to determine whether it can accurately represent polythermal density data for a binary mixed-volatile system. To do this, we plan to use Equation 6 to correlate density data for CO_2-CH_4 mixtures at 50-400°C, 9.94-99.93 MPa [19-20]. If that effort yields a highly accurate correlation, general applicability of Equation 6 to binary, supercritical mixed-volatile fluids will be strongly indicated. Finally, the versatility of Equation 6 would be tested severely in any attempt to use it to model the thermodynamic behavior of subcritical mixed-volatile fluids. In this circumstance, excess volumetric properties and liquid-vapor phase relations must be well represented.

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Fig. 1. Experimentally determined (Seitz and Blencoe [10]) and calculated (this study) excess molar volumes for CO₂-H₂O fluids at: (a) 400°C—9.94, 14.94, 19.94, 24.94 and 29.94 MPa; and (b) 400°C—29.94, 34.94, 39.94, 49.93, 59.93, 79.93 and 99.93 MPa. Error bars are shown for one data point at pressures from 9.94 to 39.94 MPa. Error bars for pressures from 49.93 to 99.93 MPa are too small to be seen at the scale of the plot. In a given isobaric data set, all excess molar volumes have similar uncertainties.
Fig. 2. Experimentally determined (Sterner and Bodnar [12]) and calculated (this study) excess molar volumes for CO₂-H₂O fluids at 400°C, (a) 200 MPa, (b) 300 MPa, and (c) 400 MPa.