Accurate Calculation of Thermodynamic Properties of H$_2$O-CO$_2$-CH$_4$ Single and Binary Fluids in P-T Ranges of Geothermal Interest

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ABSTRACT

Duan, et al. (1992a, 1992b) developed an equation of state (EOS), similar to that of Lee and Kesler (1975), that describes P-V-T-X relations in the system H$_2$O-CO$_2$-CH$_4$ over the range 50-1000 °C / 0–1000 bar (0-1000 °C / 0-8000 bar for single component fluids). An extensive comparison of values calculated with this EOS and experimental P-V-T-X and solvus data was published by Nieva and Barragán (2003).

The equation of state, which will be referred to as DMW EOS, was integrated in order to calculate thermodynamic properties of single and binary fluids in the system H$_2$O-CO$_2$-CH$_4$. Calculated values are compared with tabulated data for water, carbon dioxide and methane, as well as their binary mixtures.

For single component fluids the ability of the DMW EOS to reproduce tabulated data decreases, as expected, from the nonpolar component to the condensed phase of the more polar component (pressurized liquid water). In a range of interest for the analysis of middle to high temperature hydrothermal systems (125 – 375 °C), tabulated specific enthalpy data for methane, carbon dioxide and superheated steam may be reproduced within ± 6, ± 9 and ± 54 KJ/Kg, respectively. Published enthalpy data for H$_2$O – CO$_2$ and H$_2$O – CH$_4$ fluids may be reproduced within ± 11 and ± 25 KJ/Kg. In more limited ranges (170 – 370 °C for steam and 240 – 370 °C for liquid), published enthalpy data for saturated steam and liquid water may be reproduced within ± 76 and ± 45 KJ/Kg, respectively.

1. INTRODUCTION

Water, carbon dioxide and methane are among the most important constituents of crustal fluids, and knowledge of their thermophysical properties has proved useful for the analysis of the thermal evolution of geological formations (see for example Roedder, 1984; Ramboz et al., 1985). Their geological importance has fostered studies of the P-V-T-X and solvus properties of binary fluids in the H$_2$O-CO$_2$-CH$_4$ system for decades (see for example Blencoe et al., 1999; Seitz and Blencoe, 1999; Fenghour et al., 1996; Joffrion and Eubank, 1989; Zakirov, 1984; Takenouchi and Kennedy, 1964; Tödheide and Franck, 1963; Malinin, 1959; Donnelly and Katz, 1954).

Duan, et al. (1992a, 1992b) developed an equation of state (EOS), similar to that of Lee and Kesler (1975), that describes P-V-T-X relations in the system H$_2$O-CO$_2$-CH$_4$ over the range 50-1000 °C / 0–1000 bar (0-1000 °C / 0-8000 bar for single component fluids). An extensive comparison of values calculated with this EOS and experimental P-V-T-X and solvus data was done by Nieva and Barragán (2003).

In this contribution, the above equation of state is integrated and its ability to reproduce published thermodynamic properties of single-component and binary (H$_2$O-CO$_2$; H$_2$O-CH$_4$) fluids is examined for the particular range of interest for moderate and high temperature hydrothermal systems.

2. EQUATION OF STATE

The Duan et al. (1992a, 1992b) equation of state, which will be referred to as the DMW EOS, may be written as follows:

\[
Z = \frac{PV}{RT} = 1 + \frac{BV}{V^2} + \frac{CV^2}{V^2} + \frac{DV^4}{V^4} + \frac{EV^5}{V^5} + \frac{FV^2}{V^2} \exp(\frac{-FV^2}{V^2})
\]

where \(Z\) is the compressibility factor, \(P\) is pressure in bars, \(T\) is absolute temperature and \(V\) is specific volume in liter/mol. \(R\) is the ideal gas constant. The parameters \(B, C, D\) and \(E\) are defined by equations of the form:

\[
B = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2}
\]

the parameter \(F\) is given by

\[
F = \frac{\alpha}{T_c^3}
\]

\(V_c\), which is not the critical volume, is a function of the critical temperature and pressure

\[
V_c = \frac{RT}{P_c}
\]

and \(T_c\) is the reduced temperature (T/T_c).

Values for the component-specific parameters \(a_1, \ldots, \alpha, \beta\) and \(\gamma\) are given by Duan et al. (1992a).

In the application of Eqn. 1 to mixtures, Duan et al. (1992b) utilize the mixing rule proposed by Benedict et al. (1942), modified (following Anderko and Pitzer, 1991) with the introduction of second and third order adjustable parameters. Thus, the expression:
\[ Q = \left( \sum \chi_i Q_i^{1/3} \right)^3 \]  

(5)

where \( Q \) represents the ith single-component value is used to obtain the mixture value in the case of parameters D, E and F. Temperature dependent second and third order adjustable parameters are utilized to evaluate B, C and \( \gamma \) for binary fluids.

The mixing rule expressions and those for the binary interaction parameters for H\(_2\)O-CO\(_2\), H\(_2\)O-CH\(_4\) and CO\(_2\)-CH\(_4\) mixtures are described by Duan et al. (1992b).

3. CALCULATION OF THERMODYNAMIC PROPERTIES

P-V-T data allows the calculation of residual functions:

\[ M^R(T, P) = M(T, P) - M^*(T) \]

(6)

where \( M^R \) and \( M^* \) stand for the reduced and ideal property, respectively.

Expressions for the compressibility factor, such as Eqn. 1, also allow the calculation of residual functions, provided their partial derivatives describe correctly the dependence of \( Z \) with respect to temperature.

It can be shown (see for example, Hall et al., 1983) that:

\[ A^R = RT \int_0^{\rho} \frac{(Z - 1)}{\rho} d\rho - \ln Z \]

(7)

and

\[ U^R = R \int_0^{\rho} \left( \frac{\partial Z}{\partial (1/T)} \right) d\rho \]

(8)

The integral in Eqn. 7 is trivial, since the compressibility factor is explicit in the density. The resulting expression is:

\[ \frac{A^R}{RT} = B\rho_t + C\rho_t^2 + D\rho_t^4 + E\rho_t^5 - \left( \frac{F}{\gamma} \right) (\beta + 1) \exp\left( -\frac{\rho_t^2}{\gamma} \right) \]

\[ - \left( \frac{F}{2\gamma} \right) \left( \beta + 1 \right) - \ln \frac{Z}{RT} \]

(9)

where we have used the notation:

\[ \rho_t = \frac{V_e}{V} ; \quad B\rho_t = \frac{BV_e}{V} ; \quad C\rho_t^2 = \frac{CV_e^2}{V^2} \]

an so on.

The integral in Eqn. 8 is more complicated because it involves the derivative with respect to temperature of the parameters B, C, D, E, F, \( \gamma \), and, for the case of binary fluids also the temperature derivatives of the binary interaction parameters. The resulting expression is:

\[ \frac{U^R}{RT} = B'\rho_t + C'\rho_t^2 + D'\rho_t^4 + E'\rho_t^5 - \left( \frac{F'\beta}{2\gamma} + (F'\gamma + F'\gamma - F'\gamma) \left( \frac{\rho_t^2}{2\gamma} + \frac{1}{2\gamma^2} \right) \right) \]

\[ - \left( \frac{F'\gamma}{2\gamma^2} + \frac{F'\gamma}{2\gamma^2} (\beta + 1) - \frac{F\beta\gamma}{2\gamma^2} \right) \]

(10)

where \( B' \), \( C' \), etc. are derivatives with respect to the reciprocal of the absolute temperature.

The ideal gas properties of each component may be obtained from the ideal heat capacities, as follows:

\[ E^* = \int_0^T C_v^* dT \]

(11)

and

\[ S^* = \int_0^T C_p^* dT \]

(12)

where the ideal specific heat capacities at constant volume and pressure are related by the expression:

\[ C_p^* = C_v^* + R \]

(13)

The ideal specific heat capacity at constant volume in the case of nonlinear molecules is given by:

\[ C_v^* = 3R + \sum_{i=0}^\infty R \left( \frac{T_{\text{vib}}}{2T} \right)^2 \sinh^{-2} \left( \frac{T_{\text{vib}}}{2T} \right) \]

(14)

and for linear molecules by:

\[ C_v^* = \frac{5}{2}R + \sum_{i=0}^\infty R \left( \frac{T_{\text{vib}}}{2T} \right)^2 \sinh^{-2} \left( \frac{T_{\text{vib}}}{2T} \right) \]

(15)

where the summations are over the values of the characteristic vibrational temperatures (\( T_{\text{vib}} \)) of the molecule. Values of the characteristic vibrational temperatures for H\(_2\)O, CO\(_2\) and CH\(_4\), are given by Callen (1960).

Eqns. 14 and 15 include the contributions to the heat capacity of the translational, rotational and vibrational modes, and are accurate up to a temperature above which contributions from electronic transitions between molecular orbitals become significant (ca 10,000 K).
The resulting expressions for the ideal internal energy and entropy applicable to H₂O and CH₄ (i.e. nonlinear molecules) are:

\[ U^* = 3RT + R \sum_{i} \frac{T_{vib}}{\exp(T_{vib}/T)} \]  

(16)

and

\[ S^* = 4R \ln T + \sum_{i} \left[ \frac{T_{vib}}{4T} \exp\left(-\frac{T_{vib}}{T}\right) - \left(\frac{1}{4}\right) \ln(1 - \exp(-\frac{T_{vib}}{T})) \right] \]  

(17)

whereas for CO₂ they are given by expressions similar to Eqs. 16 and 17, but with the subtraction of \((1/2)RT\) and \((1/2)R\ln T\), respectively.

The ideal Helmholtz free energy may then be obtained by the relation:

\[ A^* = U^* - TS^* \]  

(18)

From the reduced and ideal internal energy (and Helmholtz free energy) one may obtain the internal energy (and Helmholtz free energy) for the real gas from Eqn. 6. All other thermodynamic functions may be obtained from A and U.

4. COMPARISON WITH PUBLISHED DATA

Setzmann and Wagner (1991) presented an extensive tabulation of thermodynamic properties for methane, as calculated with their equation of state. The DMW EOS, through the formulae described above, reproduces their calculated values of enthalpy in the range 7-350 °C / 0.25-2000 bar through the formulae described above, reproduces their calculated values of enthalpy in the range 7-350 °C / 0.25-2000 bar. The DMW EOS, through the formulae described above, reproduces their calculated values of enthalpy in the range 7-350 °C / 0.25-2000 bar. The DMW EOS, through the formulae described above, reproduces their calculated values of enthalpy in the range 7-350 °C / 0.25-2000 bar.

Patel and Eubank (1988) reported the thermodynamic properties of H₂O-CO₂ mixtures over the range 50-225 °C / 0.9-100 bar / 0.02-0.5 XH₂O, which were calculated from experimental densities. For fluids with less than 10% molar content of water, the DMW EOS invariably underestimates the published value for enthalpy, with an error spread of 3 percentage units, centered at -3%, except for cases at the extreme temperature and pressure limit for each composition where deviations are larger but never exceeding 6 percentage units. For fluids with lower water content (25 and 50 molar percent), deviations show a spread of about 3.5 percentage units, centered about -2%, except for cases at the extreme temperature and pressure limit for XH₂O = 0.25 where deviations are larger but never exceeding 6.8 percentage units.

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Joyce and Blencoe (1994) measured the fugacity of H₂O in water-carbon dioxide mixtures at 500 bar in the range 400-700 °C, and calculated the activity of water from the expression:

\[ a_{H₂O} = \frac{f_{H₂O}}{f_{H₂O}^°} \]  

(19)

where \(f_{H₂O}^°\) and \(f_{H₂O}\) represent the fugacity of the ith component by itself and in the mixture, respectively, at the same conditions of pressure and temperature.

The DMW EOS reproduces these activity values within the experimental error in the high water fraction range (XH₂O>0.4), and underestimates the measured values at lower water contents; the underestimation is larger at the lower end of the temperature range (see Fig. 1).

Excess values of thermodynamic parameters in a gas mixture are defined as their value in the mixed system minus their value in a system comprised by the corresponding amounts of the unmixed gases. Wormald and Colling (1984) measured excess molar enthalpies in H₂O-CH₄ fluids at 180 – 425°C / 3 – 12.6 MPa / XH₂O = 0.3 – 0.7. For temperatures in the range 180-325°C the DMW EOS reproduces the excess enthalpy values with deviations smaller than 290 J/mol, which represent deviations of the system’s enthalpy smaller than 2.4% for all pressures and compositions. At 425 °C, all pressures and XH₂O = 0.5 it invariably underestimates the experimental values, with very small deviations at low pressures, and deviations up to –3.5% of the system’s enthalpy at 126 bar. Performance at 375 °C is particularly complex, with the DMW EOS invariably underestimating the experimental values, and with deviations of system’s enthalpy increasing with pressure, reaching up to ~12% at 126 bar. This contrasting above 275 °C, and is increasingly overestimated below this temperature; overestimation is within 4.1% down to 250 °C, within 10% down to 220 °C, and grossly increases below this temperature. The enthalpy of compressed liquid in the pressure range of 25-1000 bar is reproduced within ±6% for temperatures above 240 °C; for temperatures below 180 °C it is grossly overestimated.

Joffrion and Eubank (1989) calculated thermodynamic properties of H₂O-CH₄ mixtures over the range 125-225 °C / 0.7-120 bar / 0.1-0.5 XH₂O from experimental densities. The DMW EOS reproduces the published values within 1%, except at the low temperature / high pressure limit for each composition, where deviations are larger but never exceeding 3.4%. The deviation distribution is about the same for all compositions.

The resulting expressions for the ideal internal energy and entropy applicable to H₂O and CH₄ (i.e. nonlinear molecules) are:

\[ U^* = 3RT + R \sum_{i} \frac{T_{vib}}{\exp(T_{vib}/T)} \]  

(16)

and

\[ S^* = 4R \ln T + \sum_{i} \left[ \frac{T_{vib}}{4T} \exp\left(-\frac{T_{vib}}{T}\right) - \left(\frac{1}{4}\right) \ln(1 - \exp(-\frac{T_{vib}}{T})) \right] \]  

(17)

whereas for CO₂ they are given by expressions similar to Eqs. 16 and 17, but with the subtraction of \((1/2)RT\) and \((1/2)R\ln T\), respectively.

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From the reduced and ideal internal energy (and Helmholtz free energy) one may obtain the internal energy (and Helmoltz free energy) for the real gas from Eqn. 6. All other thermodynamic functions may be obtained from A and U.
behavior at 375 °C is attributed to the vicinity of a discontinuity in the temperature dependence of the second order H₂O-CH₄ interaction parameter.

Figure 1: Activity of water vs molar fraction of water in H₂O-CO₂ fluids at 50 MPa and 678.2 K. The solid line is calculated with the DMW EOS. The closed circles represent data from Joyce and Blencoe (1994). The vertical bars represent the experimental uncertainty.

Blencoe et al. (1999) calculated excess Gibbs free energies of H₂O-CO₂ mixtures from experimental density data measured at 400 °C : 0–400 MPa (Seitz and Blencoe, 1999) and P-V-T-X data from synthetic fluid inclusions (Sterner and Bodnar, 1991). Excess Gibbs free energies calculated with the DMW EOS show the same qualitative trends than the values calculated by Blencoe et al. (1999), namely continuous positive values asymmetric toward H₂O, and maxima increasing with pressure. Fig. 2, which is to be compared with Fig. 6a of Blencoe et al. (1999), shows the excess Gibbs free energy as a function of the molar fraction of carbon dioxide. The DMW EOS gives maxima of 1171 and 1429 J/mol at 50 and 100 MPa, respectively, as compared with values of 1300 and 1800 J/mol reported by those authors. These differences in value of excess Gibbs free energy represent underestimations of the order of about 4.4% with respect to the Gibbs free energy of the gas mixture.

Smith and Wormald (1984) measured excess molar enthalpies of H₂O-CO₂ fluids at one atmosphere in the range 90-120 °C / 0.416-0.645 X_H₂O. The DMW EOS invariably overestimates these values by differences smaller than 75 J/mol, constituting differences of less than 1.1 % of the enthalpy of the system.

Wormald et al. (1986) measured excess molar enthalpies in the same system at X_H₂O = 0.5 in the range 175-425 °C / 0.44-13.4 MPa. At each experimental temperature the deviations increase with the experimental pressure. At temperatures in the range 175-225 °C the deviation of system’s enthalpy is smaller than 1.5%. For temperatures in the range 250-275 °C deviations are smaller than 3.1%. For temperatures of 300 °C and 325°C, deviations are smaller than 3.1% at pressures lower than 67 bar and 88 bar, respectively; deviations are larger at higher pressures, but never exceeding 4.8%. At 375 °C deviations are within 1.5% at all pressures. At the temperature of 425 °C the system’s enthalpy is grossly underestimated at all pressures above 1.6 MPa. This is in sharp contrast with the relatively good reproduction of the system’s Gibbs free energy derived from Blencoe et al. (1999) values of excess Gibbs free energy, at similar temperatures and even higher pressures. See next section for further discussion on this point.

5. DISCUSSION

On the basis of an extensive comparison with published volumetric and solvus data, Nieva and Barragán (2003) determined the regions of best applicability of the DMW EOS. In general, the equation of state behaves best at conditions well removed from the boundaries of its nominal range of applicability (pressures close to 1000 or 50 bar; temperatures close to 50 °C), and for H₂O-CO₂ fluids also removed from the vicinity of the critical curve (as defined by data from Takenouchi and Kennedy, 1964). For binary fluids, an important source of error derives from the discontinuities in the temperature dependence of the binary interaction parameters; in fact, the derivative with respect to temperature does not exist at those discontinuities. As suggested by Nieva and Barragán (2003), a possible means for solving the problems associated with those discontinuities is to perform a series of calculations on both sides and interpolating.

As expected, the DMW EOS behaves best when applied to the simplest single-component fluid (methane) and worst for the condensed phase of the more complex component (saturated and pressurized liquid water).

In the range 7 – 350 °C / 0.25-2000 bar, the DMW EOS is able to calculate the enthalpy of methane tabulated by Setzmann and Wagner (1991) within ± 11 KJ/Kg, which represents ± 1.85% of a “median” enthalpy value (600 KJ/Kg).

The DMW EOS tends to underestimate the enthalpy of CO₂ (as reported by Sweigert et al., 1946). The tabulated values for the range 10 – 790 °C / 0.014 – 210 bar are reproduced with an error distribution centered at -34 KJ/Kg. The width of the error distribution is ± 46 KJ/Kg, which represents ± 5.2% with respect to a median enthalpy value (890 KJ/Kg).

The DMW EOS invariably underestimates the enthalpy of superheated steam in the range 120 – 1000 °C / 1 – 100 bar (as tabulated by Keenan et al., 1978), with an error distribution centered at -77 KJ/Kg. The width of the error distribution is ± 54 KJ/Kg, which represents ± 1.7% with respect to a median enthalpy value (3200 KJ/Kg).

In the range 170 – 370 °C, the DMW EOS reproduces the tabulated enthalpy of saturated steam with an error distribution centered at 25 KJ/Kg, and an error width of ± 76 KJ/Kg, which represents ± 2.9% with respect to a median enthalpy value (2600 KJ/Kg). In a more limited range (240 – 370 °C) the tabulated values for the enthalpy of saturated liquid are reproduced with an error distribution centered at 22 KJ/Kg. The error width is ± 45 KJ/Kg, which represents ± 3% with respect to a median enthalpy value (1500 KJ/Kg).

The DMW EOS reproduces the tabulated enthalpy of pressurized liquid water in the range 240 – 380 °C with an error distribution centered at 0.5 KJ/Kg, and an error width of ± 60 KJ/Kg, which represents ± 4.3% with respect to a median enthalpy value (1400 KJ/Kg).

Tested against tabulated enthalpy data from Joffrion and Eubank (1989) and excess enthalpy data from Wormald and Colling (1984) for the system H₂O-CH₄ in the range 125 – 325 °C / 0.7 – 126 bar / X_H₂O = 0.1 – 0.5, the DMW EOS can reproduce the published values within ± 25 KJ/Kg, which represents ± 3.7% with respect to a median enthalphy value (680 KJ/Kg). The equation cannot reproduce the data from Wormald and Colling (1984) at ca 375 °C, given the

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Figure 1: Activity of water vs molar fraction of water in H₂O-CO₂ fluids at 50 MPa and 678.2 K. The solid line is calculated with the DMW EOS. The closed circles represent data from Joyce and Blencoe (1994). The vertical bars represent the experimental uncertainty.
vicinity of one of the discontinuities in the binary interaction parameter $k_{12,\text{HDO-CH}_4}$.

Tested against tabulated enthalpy data from Patel and Eubank (1988) and excess enthalpy data from Wormald et al. (1986) and Smith and Wormald (1984) for the system H$_2$O-CO$_2$ in the range 50 – 375 °C / 0.9 – 104 bar / $X_{\text{H}_2\text{O}} = 0.02 - 0.68$, the DMW EOS can reproduce the published values within ± 12 KJ/kg, which represents ± 4.6 % with respect to a median enthalpy value (240 KJ/kg).

An important observation on the behavior of the DMW EOS is its inability to reproduce the H$_2$O-CO$_2$ excess enthalpy values of Wormald et al. (1986) at 425 °C. This results from the existence of a root on the expression for the second virial coefficient for CO$_2$ (Eqn. 2) at ca 425.2 °C, which in turn leads to a singularity in its temperature derivative. However, at 400 °C the DMW EOS gives a good semi-quantitative reproduction of the excess Gibbs free energies of Blencoe et al. (1999) (see last section and Fig. 2).

![Figure 2: Excess Gibbs free energy vs molar fraction of carbon dioxide in H$_2$O-CO$_2$ fluids at 400 °C and 30, 50 and 100 MPa, as calculated with the DMW EOS. The solid line is calculated with the DMW EOS.](image)

**6. CONCLUSIONS**

In the simulation or analysis of a physical process, what matters is the difference of internal energy (and other thermodynamic functions) of the system between one equilibrium state and another. As mentioned above, an expression for the compressibility factor allows the calculation of thermodynamic properties, provided its partial derivatives describe correctly the dependence of $Z$ with respect to temperature. A major contribution of the present work is the demonstration that by using Eqn. 1 it is indeed possible to calculate the thermodynamic properties of single component fluids and binary mixtures in the ternary H$_2$O-CO$_2$-CH$_4$.

It is shown above that the DMW EOS can reproduce published values of enthalpy and Gibbs free energy of single-component (CH$_4$, CO$_2$ and H$_2$O) and binary fluids (H$_2$O-CO$_2$ and H$_2$O-CH$_4$) in substantial ranges of pressure, temperature and composition, within at worst ± 45 KJ/Kg (± 75 KJ/Kg for H$_2$O). These uncertainty ranges are considered exaggerated because they include the outliers of error distributions which are relatively narrow, and because some of the comparisons were made by calculating excess thermodynamic quantities, a process which carries the combined errors from calculations of single-components and binary fluids. The stated accuracy is enough for the semi-quantitative calculation of excess thermodynamic quantities.

In the range of interest for the analysis or simulation of phenomena in middle to high temperature hydrothermal systems (125 – 375 °C), accuracies are better (CH$_4$: ± 6 KJ/Kg; CO$_2$: ± 9 KJ/Kg; H$_2$O–CO$_2$: ± 11 KJ/Kg; H$_2$O–CH$_4$: ± 25 KJ/Kg), again with pure water as the system reproduced with the least accuracy, in fact unacceptable below 170 °C. For the simulation of a process where the fluid changes from pure water to a binary mixture, it is recommended that a suitable equation of state (or set of empirical expressions) is used for pure water, making sure that values are referred to the same standard state.

It is important to emphasize that the DMW EOS is unable to reproduce physical quantities that depend on the derivative of $Z$ with respect to temperature, around temperature values where the binary interaction parameters are discontinuous, and where a virial coefficient becomes zero.

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