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Correlation for the Carbon Dioxide and Water Mixture Based on The Lemmon–Jacobsen Mixture Model and the Peng–Robinson Equation of State

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Models representing the thermodynamic behavior of the CO_2–H_2O mixture have been developed. The single-phase model is based upon the thermodynamic property mixture model proposed by Lemmon and Jacobsen. The model represents the single-phase vapor states over the temperature range of 323–1074 K, up to a pressure of 100 MPa over the entire composition range. The experimental data used to develop these formulations include pressure–density–temperature-composition, second virial coefficients, and excess enthalpy. A nonlinear regression algorithm was used to determine the various adjustable parameters of the model. The model can be used to compute density values of the mixture to within ±0.1%. Due to a lack of single-phase liquid data for the mixture, the Peng–Robinson equation of state (PREOS) was used to predict the vapor–liquid equilibrium (VLE) properties of the mixture. Comparisons of values computed from the Peng–Robinson VLE predictions using standard binary interaction parameters to experimental data are presented to verify the accuracy of this calculation. The VLE calculation is shown to be accurate to within ±3 K in temperature over a temperature range of 323–624 K up to 20 MPa. The accuracy from 20 to 100 MPa is ±3 K up to ±30 K in temperature, being worse for higher pressures. Bubble-point mole fractions can be determined within ±0.05 for CO_2.

KEY WORDS: binary mixture; carbon dioxide; mixture equation of state; Peng–Robinson; thermodynamic properties; water.

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1. INTRODUCTION

The carbon dioxide–water mixture is of importance in the design and analysis of gas turbine systems. Rather than using air, new zero-emission gas turbines are using oxygen to burn the fuel. The products of these combustion reactions are primarily carbon dioxide and water. The CO_2–H_2O mixture must be considered at high temperatures down stream of the combustor, as well as at low temperatures during compression. Phase equilibria must also be calculated for CO_2 recapture.

According to the International Association for the Properties of Water and Steam (IAPWS) Identified Critical Research Need-14 (ICRN-14) [1], there is a need for a new equation of state for the CO_2–H_2O mixture. The best equation of state that is available was published by Gallagher et al. [2]. It is accurate from 400 to 1000 K up to 100 MPa and 30% mole fraction CO_2. IAPWS was particularly interested in expanding the mole fraction limitation.

The formulation presented is an expansion of the Lemmon–Jacobsen model [3] to include the CO_2–H_2O system. It is valid in the single-phase vapor region over the entire composition range, from 323–1074 K, up to a pressure of 100 MPa. Due to a lack of single-phase liquid data for the mixture, the Peng–Robinson equation of state (PREOS) was used to model the vapor–liquid equilibrium (VLE) properties of the mixture. VLE can be calculated at temperatures from 323 to 624 K up to 100 MPa.

2. EXPERIMENTAL DATA

Experimental data are paramount in the development of mixture models. The data are used to determine coefficients, exponents, and other parameters for the model. Table I is a summary of the single-phase experimental data for CO_2–H_2O mixtures available in the open literature. Table II summarizes the VLE dew-point data. “N/A” is used to denote when data were not provided or not recorded in tabular format. Not all of the data listed in Table I were used in the development of the formulation. Data that were used are denoted with an asterisk. All of the data, however, were compared to the formulation.

Tables I and II also contain the statistical parameter, average absolute deviation (AAD), which is defined as

$$\mathrm{AAD} = \frac{1}{n}\sum_{i=1}^{n} |\%\Delta X|, \qquad (1)$$

Table I. Single Phase Experimental Data for the CO_2–H_2O Mixture

		Temperature (K)		Pressure (MPa)		% CO_2 conc.		
Author[a]	No. Points	Low	High	Low	High	Low	High	AAD (%)
Pressure–density–temperature								[b]
Abdulagatov et al. [4]	72	673	673	10	40	0	60	3.055
*Fenghour et al. [5]	124	415	700	6	35	6	80	0.275
*Fenghour et al. [5] (dew point)	11	405	613	5.7	24	20	94	0.670
Franck and Todheide [6]	303	673	1023	30	200	20	80	5.018
Gehrig [7]	198	673	773	15	60	10	90	1.592
Greenwood [8]	869	823	1074	10	50	0	100	0.561
*Patel and Eubank [9]	297	323	498	0.027	10	2	50	0.029
*Sietz and Blencoe [10]	95	673	673	10	100	10	90	0.604
Zakirov [11]	159	573	673	5	180	20	80	2.499
Total	2128	323	1074	0.027	200	0	100	
Excess enthalpy								[c]
*Lancaster and Wormald [12]	102	448	698	0.37	13	50	50	2.755
Smith and Wormald [13]	40	363	392	0.101	0.101	31	65	8.405
Wormald and Lancaster [14]	4	363	393	45	83	50	50	9.287
*Wormald and Lloyd [15]	63	598	698	10	20	50	50	1.156
Total	209	363	698	0	83	31	65	
Second virial coefficient								[d]
Patel et al. [16]	51	323	498	N/A	N/A	50	98	1.452

[a] Data used in correlation procedures designated with a*.

[b] Average absolute deviation in density.

[c] Average absolute deviation in excess enthalpy.

[d] Difference in second virial coefficient ($dm^3 \cdot mol^{-1}$).

where $\%\Delta X$ is the percent deviation between the experimental data and the calculated property defined by

$$\%\Delta X = 100\left(\frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}}\right). \tag{2}$$

3. LEMMON–JACOBSEN MODEL

The Lemmon and Jacobsen model [3] uses pure-fluid fundamental equations and an excess function in order to predict fluid properties. A brief outline of the model development is presented here. For more detailed information, refer to Lemmon and Jacobsen [3].

Table II. VLE and Dew Point Experimental Data for CO_2–H_2O Mixtures

		Temperature (K)		Pressure (MPa)		% CO_2 conc.		
Author[a]	No. points	Low	High	Low	High	Low	High	AAD[b] (%)
Dew point								
Fenghour et al. [5] (dew point)	11	405	613	5.7	24	20	94	0.644
Patel et al. [16]	47	312	482	0.0852	8.6	50	98	1.068
Takenouchi and Kennedy [17]	89	383	623	10	150	9	96	2.524
Todheide and Franck [18]	60	323	623	20	350	12	99	2.749
Total	207	313	623	0.0852	350	9	99	

[a] All data used in correlation procedure.
[b] Average absolute deviations in temperature.

The Lemmon–Jacobsen model was developed explicitly in terms of the dimensionless Helmholtz energy, defined as

$$\alpha = \frac{A}{RT}. \tag{3}$$

The dimensionless Helmholtz energy of the mixture can be represented by

$$\alpha = \alpha_{\mathrm{m}}^{\mathrm{i}} + \alpha^{\mathrm{E}}. \tag{4}$$

In this equation, $\alpha_{\mathrm{m}}^{\mathrm{i}}$ is the dimensionless Helmholtz energy of an ideal mixture and α^{E} is the excess dimensionless Helmholtz energy.

The advantage of this model is that the term $\alpha_{\mathrm{m}}^{\mathrm{i}}$ comes directly from the fundamental equations for the pure fluids. The dimensionless Helmholtz energy of an ideal mixture can be written such that

$$\alpha_{\mathrm{m}}^{\mathrm{i}}(\delta, \tau, \mathbf{x}) = \alpha_{\mathrm{m}}^{0}(\delta, \tau, \mathbf{x}) + \sum_{i=1}^{n} x_i \alpha_i^{\mathrm{r}}(\delta, \tau). \tag{5}$$

In Eq. (5) $\alpha_{\mathrm{m}}^{0}(\delta, \tau, \mathbf{x})$ is the ideal-gas dimensionless Helmholtz energy of the mixture, given by

$$\alpha_{\mathrm{m}}^{0}(\delta, \tau, \mathbf{x}) = \sum_{i=1}^{r} x_i \left[\alpha_i^{0}(\delta, \tau) + \ln(x_i)\right], \tag{6}$$

where

$$\alpha^0(\delta,\tau)=\frac{A^0(\rho,T)}{RT}=\frac{h_0^0}{RT_c}-\frac{s_0^0}{R}-1+\ln\frac{\delta\tau_0}{\delta_0\tau}-\frac{\tau}{R}\int_{\tau_0}^{\tau}\frac{c_p^0}{\tau^2}d\tau+\frac{1}{R}\int_{\tau_0}^{\tau}\frac{c_p^0}{\tau}d\tau. \quad (7)$$

In this equation, h_0^0, s_0^0, T_0, and P_0 refer to the ideal-gas reference state with $\delta_0=P_0/(\rho_0 R T_0)$. To complete this equation, the ideal-gas isobaric heat capacity must be known.

In Eq. (5), α_i^{r} is the pure-fluid residual, which is often represented by

$$\alpha_i^{\mathrm{r}}(\delta,\tau)=\sum_{k=1}^{m}N_k\delta^{i_k}\tau^{j_k}\exp\left(-\gamma\delta^{l_k}\right). \quad (8)$$

If an equation of state is available for the pure fluids, it can be used to calculate the values for α_i^{r} and α_i^0. At this point, the ideal mixture $\alpha_{\mathrm{m}}^{\mathrm{i}}$ can be calculated by Eqs. (4)–(7).

To complete the definition of the terms in Eq. (4), it is necessary to calculate the excess reduced Helmholtz energy, which is given by

$$\alpha^{\mathrm{E}}=\sum_{p=1}^{r}\sum_{q=p+1}^{r}x_p x_q F_{pq}\sum_{k=1}^{10}N_k\delta^{i_k}\tau^{j_k} \quad (9)$$

The coefficients N_k, are obtained from a linear regression of experimental data. The exponents i_k and $j_k$are then determined by a nonlinear regression. The N_k, i_k, and j_k values remain unchanged independent of the fluid. The mole fractions of the species are represented by x_p and $x_q.F_{pq}$ is a fluid specific parameter.

Finally, the reducing parameters for δ and τ must be developed. For the Lemmon–Jacobsen model, δ and τ for the mixture are defined as

$$\delta=\rho/\rho_j,\ \text{and} \quad (10)$$

$$\tau=T_j/T, \quad (11)$$

where T_j and ρ_j are defined by

$$T_j=\sum_{p=1}^{r}x_p T_{c_p}+\sum_{p=1}^{r}\sum_{q=p+1}^{r}x_p^{\beta_{pq}}x_q\zeta_{pq}\ \text{and} \quad (12)$$

$$\rho_j=\left[\sum_{p=1}^{r}\frac{x_p}{\rho_{c_p}}+\sum_{p=1}^{r}\sum_{q=p+1}^{r}x_p x_q\xi_{pq}\right]^{-1}. \quad (13)$$

Table III. Coefficients and Exponents of Mixture Equation

k	N_k	i_k	j_k
1	$-2.45476271425 \times 10^{-2}$	1	2
2	$-2.41206117483 \times 10^{-1}$	1	4
3	$-5.13801950309 \times 10^{-3}$	1	-2
4	$-2.39824834123 \times 10^{-2}$	2	1
5	$2.59772344008 \times 10^{-1}$	3	4
6	$-1.72014123104 \times 10^{-1}$	4	4
7	$4.29490028551 \times 10^{-2}$	5	4
8	$-2.02108593862 \times 10^{-4}$	6	0
9	$-3.82984234857 \times 10^{-3}$	6	4
10	$2.69923313540 \times 10^{-6}$	8	-2

The parameters ζ_{pq}, ξ_{pq}, and β_{pq} are all used to define the shapes of the reducing parameter lines. The reducing parameters are not the same as the critical parameters and do not inhibit VLE calculations above the reducing temperature [19]. The parameters ζ_{pq}, ξ_{pq}, β_{pq}, and F_{pq} are mixture-dependent parameters. When adding a new fluid to the model, these parameters must be determined by regression to experimental data for the mixture. Table III includes coefficients and exponents for Eqs. (8) – (11) as presented by Lemmon and Jacobsen [3].

The development of the mixture model is predicated on having pure-fluid fundamental equations. For this analysis the formulations of Wagner and Pruss [20] and Span and Wagner [21] were used. Wagner and Pruss [20] published a 56-term equation for H_2O, while Span and Wagner [21] published a 42-term equation for CO_2. Both equations are explicit in dimensionless Helmholtz energy and are considered the best representations of the respective pure fluids.

4. VAPOR–LIQUID EQUILIBRIUM

Due to a lack of single-phase liquid data, the Lemmon–Jacobsen model would not accurately model the complex behavior of the VLE surface for CO_2–H_2O mixtures. This led to the development of an alternative method to represent the two-phase region. The PREOS [22] was chosen. The PREOS for a mixture has the following form:

$$P = \frac{RT}{V-b} - \frac{a}{(V+\varepsilon b)(V+\sigma b)} \tag{14}$$

which expressed in terms of the compressibility factor, Z, is

$$Z = Z + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon B)(Z + \sigma\beta)}. \tag{15}$$

where

$$\beta = \frac{bP}{RT} \text{ and} \tag{16}$$

$$q = \frac{a}{bRT}. \tag{17}$$

The values of a and b for mixtures are determined by empirical mixing rules,

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij} \text{ and} \tag{18}$$

$$b = \sum_{i=1}^{n} x_i b_i, \tag{19}$$

with,

$$a_{ij} = (1 - k_{ij})\sqrt{(a_i a_j)}. \tag{20}$$

where the x values in Eqs. (18) and (15) are mole fractions. The binary interaction parameter k_{ij} for CO_2–H_2O was determined to be 0.065 by a linear regression of available VLE data. By definition k_{ij} is zero for an ideal mixture. The pure fluid values of a_i and b_i are found by

$$a_i = \Psi \alpha_i(T_{ri}) \frac{\mathrm{R}^2 T_{ci}^2}{P_{ci}} \text{ and} \tag{21}$$

$$b_i = \Omega \frac{RT_{ci}}{P_{ci}} \tag{22}$$

with,

$$\alpha_i(T_{ri}) = [1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2)(1 - T_{ri}^{0.5})]^2 \tag{23}$$

where

$$T_{ri} = \frac{T}{T_{ci}}. \tag{24}$$

The constants published by Peng and Robinson [22] are listed in Table IV. Fluid specific constants are listed in Table V.

Table IV. Constants for Peng–Robinson Equation of State

Symbol	σ	ε	Ω	Ψ	Z_c
Value	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07779	0.45724	0.30740

Table V. Fluid Specific Constants

Fluid	T_{ci} (K)	P_{ci}(MPa)	ω_i
CO_2	304.2	7.376	0.225
H_2O	647.096	22.05	0.344

Vapor–liquid equilibrium (VLE) is defined when

$$\hat{\phi}_i^l x_i = \hat{\phi}_x i^v y_i \tag{25}$$

where $\hat{\phi}_i$ represents the fugacity coefficient of the i-th component in the mixture, and superscripts l and v represent the liquid and vapor phases in equilibrium, respectively.

Smith et al. [23] derived the following expression for the component fugacity coefficient, $\hat{\phi}_i$:

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-\beta) - \overline{q_i} I \tag{26}$$

where

$$\overline{q_i} = q\left(1 + \frac{\overline{a_i}}{a} - \frac{\overline{b_i}}{b}\right), \tag{27}$$

$$I = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{Z+\sigma\beta}{Z+\varepsilon\beta}\right), \tag{28}$$

$$\overline{a_i} = \left[\frac{\partial(na)}{\partial n_i}\right], \text{ and} \tag{29}$$

$$\overline{b_i} = \left[\frac{\partial(nb)}{\partial n_i}\right]. \tag{30}$$

Application of Eq. (29) to Eqs. (18) and (20) yields

$$\overline{a_i} = 2\sum_{j=1}^{n} x_j \sqrt{a_i a_j}(1-k_{ij}) - a. \tag{31}$$

Table VI. Mixture Parameters for Carbon-Dioxide and Water

F_{pq}	ξ_{pq}	ζ_{pq}	β_{pq}
5.461671501	2.4025883×10^{-2}	−302.4915666	0.974144949

Likewise, application of Eq. (30) to Eq. (19) yields

$$\overline{b_i} = b_i \tag{32}$$

5. RESULTS FOR THE SINGLE-PHASE REGION

The four adjustable fluid-specific parameters were determined for the Lemmon–Jacobsen model. These parameters were determined using a nonlinear regression algorithm, with the selected experimental data detailed in Section 2. Table VI lists the values of these parameters for the CO_2–H_2O mixture. The specific data sets used in the regression were detailed in Section 2, and they are indicated in Table I. Figures 1–3 show deviation plots of property values computed with the mixture model compared to exper-

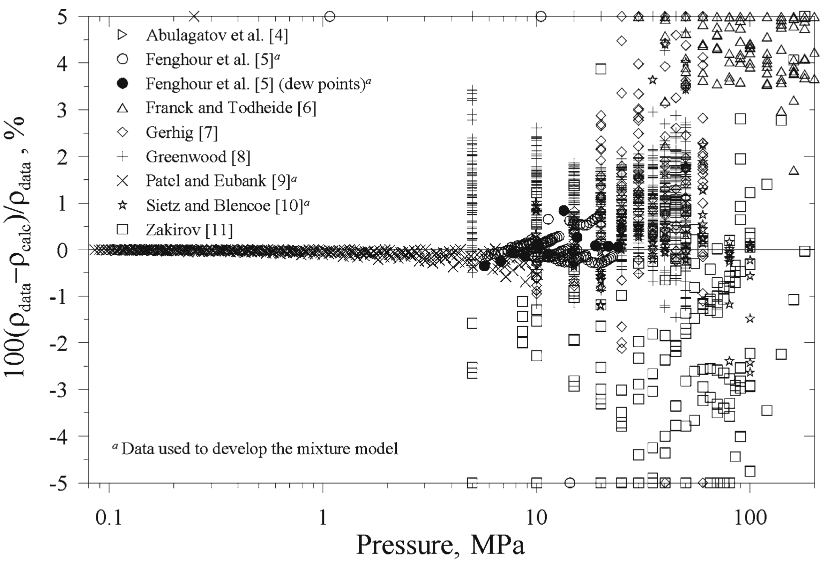

Fig. 1. Comparison of density values calculated from the mixture model to experimental data for the CO_2–H_2O mixture. The data span a temperature range of 323–1074 K and mole fractions of CO_2 ranging from 0.0 to 1.0.

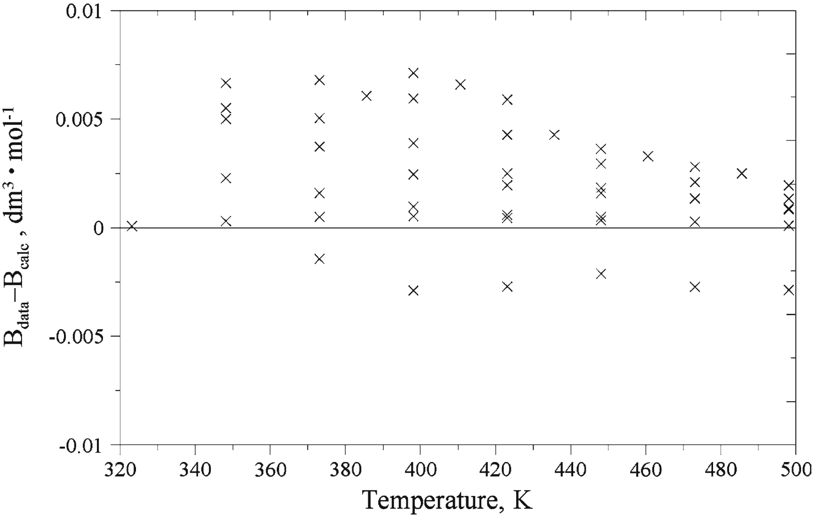

Fig. 2. Comparison of second-virial-coefficient values calculated from the mixture model to experimental data of Patel and Eubank [9] for the CO_2–H_2O mixture. The data span a temperature range of CO_2 mole fractions ranging from 0.0 to 1.0. None of these data were used in the development of the mixture model.

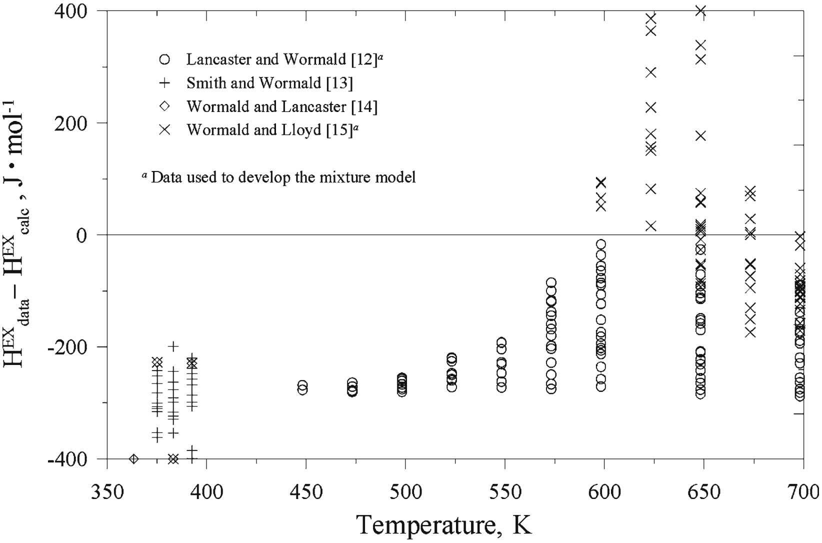

Fig. 3. Comparison of excess-enthalpy values calculated from the mixture model to single-phase experimental data for the CO_2-H_2O mixture. The data span a pressure range of 0.04–20 MPa and mole fractions of CO_2 ranging from 0.4 to 0.6.

imental data. All points plotted on the upper or lower limits can be considered to be "off-scale" and are plotted for reference only.

6. RESULTS FOR VAPOR–LIQUID EQUILIBRIUM

Figures 4 and 5 show comparisons of VLE properties computed from the Peng–Robinson equation of state to experimental data. These figures are based upon calculations carried out using an iterative solver developed by Sandler [24]. Figure 4 shows the comparison of calculated dew point temperatures to experimental data. Figure 5 shows the comparison of calculated dew point mole fractions to experimental data. The results given by this solving routine compare closely with the results determined by the regression routine that was used to compute the binary interaction coefficient ($k_{ij} = 0.065$). The temperature and liquid concentrations were calculated from an input of pressure and vapor concentration. Other comparisons could be made, but it was most important to represent the dew-point side of the VLE surface, since the single-phase model is valid only in the vapor phase.

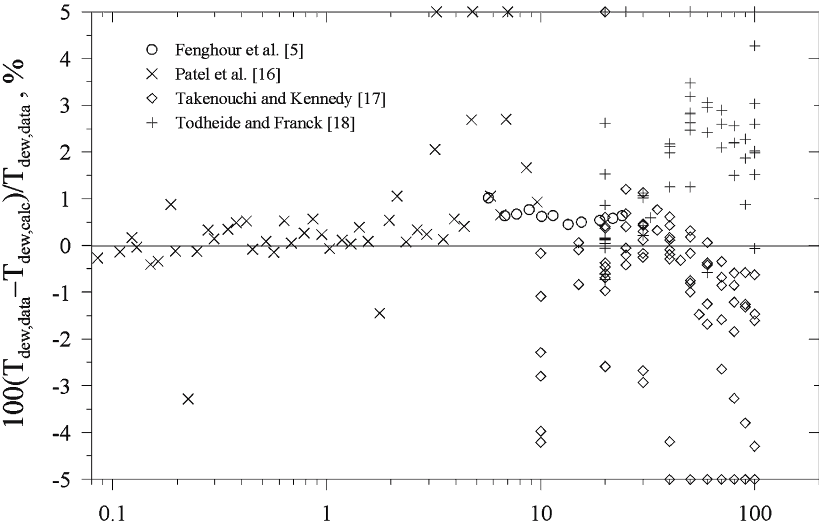

Fig. 4. Comparison of dew-point-temperature values calculated from the mixture model to experimental data for the CO_2–H_2O mixture. The data span a temperature range of 312–620 K and mole fractions of CO_2 ranging from 0.06 to 0.99. All of these data were used in the development of the mixture model.

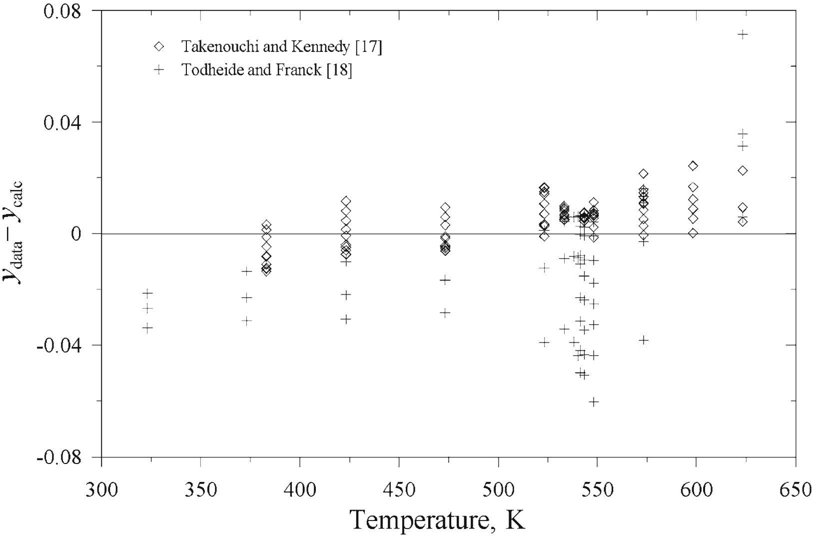

Fig. 5. Comparison of dew-point-mole-fraction values calculated from the mixture model to experimental data for the CO_2–H_2O mixture. The data span a temperature range of 10–100 MPa and mole fractions of CO_2 ranging from 0.06 to 0.99. All of these data were used in the development of the mixture model.

7. DISCUSSION OF RESULTS

The Lemmon–Jacobsen single-phase model developed in this work represents the experimental data within the reported uncertainties. Estimated uncertainties are reported in Table VII.

The only data available that included dew point densities were those by Fenghour et al. [5]. These data have a temperature range of 405–613 K and a pressure range of 5.7–24 MPa. There is a gap in the data that exists from 24 MPa and up along the dew-point line in the single-phase region. The data of Seitz and Blencoe [10] cover a temperature of 673 K up to a pressure of 100 MPa. It can be concluded from existing data that there

Table VII. Uncertainty Estimates for Single-Phase Properties

Property	Estimated Uncertainty
Density	±0.1%
Second virials	±2%
Excess enthalpy	±3%

exist enough data near the dew point above 24 MPa to be confident that the model will maintain its accuracy within this region. This can only be verified further by additional data. Greenwood [8] reported compressibility data, but in fact, the data were from a correlation of measured values and were not used in the fit. The data of Greenwood [8] had an AAD of 1.064%, which is within the 1.5% reported uncertainty. This gives a strong argument for the ability of the model to extrapolate into regions, where there are not any data, to the desired accuracies.

The single-phase model successfully predicts thermodynamic properties of the CO_2–H_2O system over the temperature range of 323–1074 K, up to a pressure of 100 MPa, and over the entire composition range in the vapor phase. Although the model here was only compared to a binary mixture, other fluids could be added. The current model also compares well to most of the other fluids calculated using the Lemmon–Jacobsen model.

The VLE calculation is estimated to be accurate to within ±3 K in temperature over a temperature range of 323–624 K up to 20 MPa. At pressures from 20 to 100 MPa, the difference between the calculated temperatures and the experimental temperatures was ±3 K up to ±30 K. It appears that deviations in temperature at higher-pressure calculations are due to the PREOS being less reliable than a wide-range fundamental equation in this region. Once the dew-point pressure, temperature, and concentration are established, the single-phase model can be used to calculate any of the remaining thermodynamic properties.

Further research should include the following:

- VLE measurements should be made at low pressure due to a lack of experimental data.
- Measurements of PVTx data above 50 MPa should be made due to a lack of experimental data.
- Measurements should be made of sound speed or c_P values to assure accurate representation of the properties that require higher-order derivatives.
- Comparisons to CO_2–H_2O–N_2 data should be made for systems where air is used in the combustion reaction.
- Measurements of liquid-phase data should be made, so that the model can be expanded to include the liquid region.

REFERENCES

1. R. Span and M. Hiegemann, *Thermophysical Properties of Humid Air and Combustion Gas Mixtures,* ICRN-14, http://www.iapws.org/ (1998).

2. J. S. Gallagher, R. Crovetto, and J. M. H. Levelt-Sengers, *J. Phys. Chem. Ref. Data* **22**:431 (1993).
3. E. W. Lemmon and R. T Jacobsen, *Int. J. Thermophys.* **20**:825 (1999).
4. I. M. Abdulagatov, A. R. Bazaev, A. E. Ramazanova, and R. K. Gasnov, *Proc. 12th Int. Conf. Prop. Water and Steam*, Orlando, Florida (1994).
5. A. Fenghour, W. A. Wakeham, and J. T. R. Watson, J. *Chem. Thermodyn*. **28**:433 (1996).
6. E. U. Franck and K. Todheide, *Z.Physik. Chem.* **22**:232 (1959).
7. M. Gehrig, *Doctoral Dissertation* (Hochschulverlag, Freiburg, 1980).
8. H. J. Greenwood, *Am. J. Sci.* **267**:191 (1969).
9. M. R. Patel and P. T. Eubank, *J. Chem. Eng. Data* **33**:185 (1988).
10. J. C. Seitz and J. G. Blencoe, *Geochim. Cosmochim. Acta* **63**:1559 (1999).
11. I. V. Zakirov, *Geokhimiya* **6**:805 (1984).
12. N. M. Lancaster and C. J. Wormald, *J. Chem. Eng. Data* **35**:11 (1990).
13. G. R. Smith and C. J. Wormald, *J. Chem. Thermodyn.* **16**:543 (1984)
14. C. J. Wormald and N. M. Lancaster, *J. Chem. Soc. Faraday Trans. 1* **84**:3141 (1988).
15. C. J. Wormald and M. J. Lloyd, *J. Chem. Thermodyn.* **26**:101 (1994).
16. M. R. Patel, J. C. Holste, K. R. Hall, and P. T. Eubank, *Fluid Phase Equilib.* **36**:279 (1987).
17. S. Takenouchi and G. C. Kennedy, *Am. J. Sci.* **262**:1055 (1964).
18. K. Todheide and E. U. Franck, *Z. Phys. Chem*. **37**:387 (1963).
19. E. W. Lemmon, *Doctoral Dissertation* (University of Idaho, Moscow, Idaho, 1996).
20. W. Wagner and A. Pruss, *J. Phys. Chem. Ref. Data* **31**:387 (2002).
21. R. Span and W. Wagner, *J. Phys. Chem. Ref. Data* **25**:1509 (1996).
22. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.* **15**:59 (1976).
23. J. M. Smith, H. C. Van Ness, and M. M. Abbott, *Chemical Engineering Thermodynamics*, 6th Ed. (McGraw Hill, New York, 2001).
24. S. Sandler, *Chemical and Engineering Thermodynamics*, 3rd Ed. (John Wiley and Sons, New York, 1999).