New Equations of State for Binary Hydrogen Mixtures Containing Methane, Nitrogen, Carbon Monoxide, and Carbon Dioxide

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New Equations of State for Binary Hydrogen Mixtures Containing Methane, Nitrogen, Carbon Monoxide, and Carbon Dioxide



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ABSTRACT

New equations of state for the binary mixtures $H_2 + CH_4$, $H_2 + N_2$, $H_2 + CO_2$, and $H_2 + CO$ are presented. The results are part of an ongoing research project aiming at an improvement of the GERG-2008 model for the description of hydrogen-rich multicomponent mixtures. The equations are formulated in terms of the reduced Helmholtz energy and allow for the calculation of all thermodynamic properties over the entire fluid surface including the gas phase, liquid phase, supercritical region, and equilibrium states. The mathematical structure of the new mixture models corresponds to the form chosen for the reference model GERG-2008 of Kunz and Wagner [J. Chem. Eng. Data 57, 3032 (2012)]. In this way, the equations can be implemented into the existing framework of the GERG-2008 model. The ranges of validity of the new equations correspond to the normal and extended ranges of validity of the GERG-2008 model.

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Key words: equation of state; Helmholtz energy; hydrogen; mixture model; thermodynamic properties.

CONTENTS

1.	Introduction	2
2.	Fundamental Equations of State for Mixtures	2
	2.1. Mathematical approach	2
	2.2. Optimization algorithm	3
3.	Results for Binary Mixtures	4
	3.1. Methane + hydrogen (CH ₄ + H ₂)	5
	3.2. Nitrogen + hydrogen $(N_2 + H_2) \dots \dots \dots$	9
	3.3. Carbon monoxide + hydrogen (CO + H_2)	11
	3.4. Carbon dioxide + hydrogen $(CO_2 + H_2)$	14
4.	Physical Behavior	17
5.	Conclusion	20
6.	Supplementary Material	21
	Acknowledgments	21
	Data Availability	21
7.	References	21

List of Tables

1	I. Molar mass and critical parameters of the pure-fluid	
	equations	4
2	2. Binary-specific reducing parameters; cf. Eqs. (6)	
	and (7)	4
3	B. Binary-specific parameters of the departure functions;	
	cf. Eq. (10)	5
4	AADs (in mol %) of VLE data calculated with the new model	
	and with GERG-2008 ⁴ for the binary system $CH_4 + H_2$	6
5	5. AARDs and AADs of homogeneous data calculated with the	
	new model and with GERG-2008 4 for the binary system CH_4	
	+ H ₂	6
6	5. AADs (in mol %) of VLE data calculated with the new model	
	and with GERG-2008 4 for the binary system N_2 + $H_2 \ldots$	9
7	7. AARDs and AADs of homogeneous data calculated with	
	the new model and with GERG-2008 ⁴ for the binary	
	system $N_2 + H_2 \dots \dots \dots \dots$	10

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8.	AADs (in mol %) of VLE data calculated with the new model	
	and GERG-2008 ⁴ for the binary system CO + H_2	13
9.	AARDs and AADs of homogeneous data calculated with	
	the new model and with GERG-2008 ⁴ for the binary	
	system CO + H_2	14
10.	AADs (in mol %) of VLE data calculated with the new model	
	and with GERG-2008 [*] for the binary system $CO_2 + H_2 \dots$	16
11.	AARDs and AADs of homogeneous data calculated with	
	the new model and GERG-2008 [°] for the binary system	1.7
10	$CO_2 + H_2$	17
12.	l est values in the single-phase region for the molar com-	21
	position of hydrogen $x_{\rm H_2} = 0.4$	21
List	of Figures	
1	t r-diagram showing the phase boundary of the binary	
1.	system CH ₄ + H ₂ at 153 K	4
2	<i>p</i> , <i>x</i> -diagram showing VLE data at 110 K. 140 K. and 170 K	
	for the binary system $CH_4 + H_2$	7
3.	Deviation of bubble-point data (top) and dew-point data	
	(bottom) from values calculated with the new EOS (left)	
	and GERG-2008 ⁴ (right) for the binary system $CH_4 + H_2$	7
4.	Percentage deviation in density in the homogeneous re-	
	gion between the new EOS and GERG-2008 ⁴ for the binary	
	system $CH_4 + H_2$	8
5.	Percentage deviation of homogeneous density data from	
	the new EOS (left) and GERG-2008 ⁴ (right) for the binary	
	system $CH_4 + H_2$	8
6.	Percentage deviation of speed of sound data from the new	
	EOS (top) and GERG-2008 ⁴ (bottom) for the binary sys-	
	tem $CH_4 + H_2$	9
7.	<i>p</i> , <i>x</i> -diagram showing VLE data at 70.4 K, 90.8 K, and 110.3	
	K for the binary system $N_2 + H_2 \dots \dots \dots \dots$	11
8.	<i>p</i> , <i>x</i> -diagram showing VLE data at 77.6 K for the binary	
	system $N_2 + H_2$	11
9.	Deviation of bubble-point data (top) and dew-point data	

(bottom) from values calculated with the new EOS (left) and with GERG-2008 4 (right) for the binary system N_2 + $H_2\,$. .

1. Introduction

Hydrogen is considered one of the most important energy carriers of the future.^{1,2} It allows for pollutant-free power generation and reduces the world's dependence on fossil fuels. Hydrogen is considered particularly important in the transport and power supply sector, which are heavily dependent on oil and other carbonaceous energy carriers such as natural gas. The injection of hydrogen into the natural-gas grid is an extensively discussed technology for a step-by-step decarbonization of heat and power supply. The electrolytic production of hydrogen using excess electricity from renewable energy sources ("power-to-gas") can contribute to a more flexible energy supply and a reduction of the demand of carbonaceous primary energy.

With increasing hydrogen content in the natural gas grid, the thermodynamic properties of the hydrogen-containing mixtures will change significantly. Recent investigations by Richter *et al.*³ have shown that the reference model GERG-2008⁴ provides reliable results for hydrogen concentrations of up to 30 mol% at typical pipeline

10.	Percentage deviation in density in the homogeneous re-	
	gion between the new EOS and GERG-2008 ⁴ for the binary	
	system $N_2 + H_2 \dots \dots$	12
11.	Percentage deviation of homogeneous density data from	
	the new EOS (left) and GERG-2008 ⁴ (right) for the binary	
	system $N_2 + H_2$	13
12.	<i>p</i> , <i>x</i> -diagram showing VLE data at 70 K, 95 K, and 125 K for	
	the binary system $CO + H_2$	14
13.	Deviation of bubble-point data (top) and dew-point	
	data (bottom) from values calculated with the new	
	EOS (left) and GERG-2008 ⁴ (right) for the binary system	
	$CO + H_2$	15
14.	Percentage deviation in density in the homogeneous re-	
	gion between the new EOS and GERG-2008 ⁴ for the binary	
	system CO + H_2	15
15.	Percentage deviation of homogeneous density data	
	from values calculated from the new EOS (top) and	
	GERG-2008 ⁴ (bottom) for the binary system $CO + H_2$.	16
16.	p, x-diagram showing VLE data at 235 K, 260 K, and	
	295.7 K for the binary system $CO_2 + H_2 \dots \dots$	17
17.	Deviation of bubble-point data (top) and dew-point data	
	(bottom) from values calculated with new EOS (left) and	
	GERG-2008 ⁴ (right) for the binary system $CO_2 + H_2$.	18
18.	Percentage deviation in density in the homogeneous re-	
	gion between the new EOS and GERG-2008 ⁴ for the binary	
	system $CO_2 + H_2$	18
19.	Percentage deviation of homogeneous density data from	
	the new EOS (left) and GERG-2008 ⁴ (right) for the binary	
	system $CO_2 + H_2$	19
20.	p , ρ -diagram (top) and p , T -diagram (bottom) calculated	
	with the new EOS in REFPROP ¹² for the binary system	
	$CH_4 + H_2$ at different compositions	20
21.	$c_{\nu}^{\rm r}$, T-diagram calculated with the new EOS in REFPROP ¹²	
	for the binary system $CH_4 + H_2$ at the equimolar compo-	
	sition and isochores up to 40 mol dm^{-3}	20
22.	p, T-diagram showing the critical curves of the binary mixtures	
	$CH_4 + H_2$, $N_2 + H_2$, $CO + H_2$, and $CO_2 + H_2$ calculated with	
	the new EOS and GERG-2008 ⁴	20

conditions. However, accurate knowledge of these properties at higher hydrogen contents is crucial not only for simulation and operation of the natural-gas grid but also in a multitude of technical processes with a wider temperature, pressure, and composition range. To provide the thermodynamic properties of hydrogen-rich mixtures with the required accuracy, new equations of state for the binary mixtures $H_2 + CH_4$, $H_2 + N_2$, $H_2 + CO_2$, and $H_2 + CO$ are presented in this work.

2. Fundamental Equations of State for Mixtures

2.1. Mathematical approach

12

The mixture models presented in this work are explicit in the Helmholtz energy *a* with the independent variables temperature *T*, density ρ , and molar composition \bar{x} . The models enable an accurate calculation of all thermodynamic properties by combining derivatives of Helmholtz energy with respect to the natural variables. A detailed summary of mathematical correlations for different thermodynamic

properties is given, e.g., in the GERG-2004 monograph.⁵ Commonly, Helmholtz equations are formulated in a dimensionless form,

$$\frac{a(T,\rho,\bar{x})}{RT} = \alpha(\tau,\delta,\bar{x}), \tag{1}$$

where α is the reduced Helmholtz energy, *R* is the molar gas constant, τ is the reciprocal reduced temperature, and δ is the reduced density. Furthermore, the Helmholtz energy is separated into an ideal part α° , which describes the behavior of the hypothetical ideal gas, and a residual part α^{r} , which considers the molecular interactions of the real fluid,

$$\alpha(\tau, \delta, \bar{x}) = \alpha^{o}(T, \rho, \bar{x}) + \alpha^{r}(\tau, \delta, \bar{x}).$$
⁽²⁾

The dimensionless ideal part of the Helmholtz energy is given by

$$\alpha^{o}(T,\rho,\bar{x}) = \sum_{i=1}^{N} x_{i} [\alpha_{o,i}^{o}(\tau_{o,i},\delta_{o,i}) + \ln x_{i}]$$
(3)

and considers the contribution of the ideal Helmholtz energy $\alpha_{0,i}^{\circ}$ of the pure components *N* according to their mole fractions x_i in the mixture. Additionally, the entropy of mixing is taken into account by $x_i \ln x_i$. The independent variables of the Helmholtz energy $\alpha_{0,i}^{\circ}$ are reduced by the respective critical properties of the pure fluids.

The residual part of the Helmholtz energy used in this work was independently developed by Lemmon, Jacobsen, and Tillner-Roth $^{6-8}$ and is defined as

$$\alpha^{\mathrm{r}}(\tau,\delta,\bar{x}) = \sum_{i=1}^{N} x_{i} \alpha_{\mathrm{o},i}^{\mathrm{r}}(\tau,\delta) + \Delta \alpha^{\mathrm{r}}(\tau,\delta,\bar{x}), \qquad (4)$$

where the first part is a linear combination of the reduced pure-fluid Helmholtz energies of all components at the corresponding state. In contrast to the ideal part, the residual part of the Helmholtz energy is reduced by common reducing properties of the resulting mixture. The reciprocal reduced temperature τ and the reduced density δ are calculated with composition-dependent reducing functions in the form proposed by Klimeck,⁹

$$\tau = T_{\rm r}(\bar{x})/T \text{ and } \delta = \rho/\rho_{\rm r}(\bar{x}) \tag{5}$$

with

$$T_{\rm r}(\bar{x}) = \sum_{i=1}^{N} x_i^2 T_{{\rm c},i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \\ \times \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \sqrt{T_{{\rm c},i} T_{{\rm c},j}}$$
(6)

and

$$\frac{1}{\rho_{\rm r}(\bar{x})} = \sum_{i=1}^{N} x_i^2 \frac{1}{\rho_{\rm c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j \beta_{\nu,ij} \gamma_{\nu,ij} \\ \times \frac{x_i + x_j}{\beta_{\nu,ij}^2 x_i + x_j} \frac{1}{8} \left(\frac{1}{\rho_{\rm c,i}^{1/3}} + \frac{1}{\rho_{\rm c,j}^{1/3}} \right)^3.$$
(7)

The adjustable binary-specific parameters β and γ allow for both symmetric and asymmetric shapes of the reducing functions. For an arbitrary order of the involved components, the following relations have to be considered:

$$\beta_{T,ij} = \frac{1}{\beta_{T,ji}}, \beta_{\nu,ij} = \frac{1}{\beta_{\nu,ji}}, \gamma_{T,ij} = \gamma_{T,ji}, \text{ and } \gamma_{\nu,ij} = \gamma_{\nu,ji}.$$
 (8)

The second part of the residual Helmholtz energy is the departure term $\Delta \alpha^{r}$. The formulation used in this work was introduced by Klimeck⁹ and further developed by Kunz *et al.*⁵ and enables an improved modeling of the non-ideal mixture behavior if an accurate database is not sufficiently described by adjusting the binary-specific interaction parameters. The departure term is given by

$$\Delta \alpha^{\mathrm{r}}(\tau, \delta, \bar{x}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha^{\mathrm{r}}_{ij}(\tau, \delta).$$
(9)

 F_{ij} is a scaling factor, which is adjusted when applying a generalized departure function or set to unity for a binary-specific departure function. For a binary system for which no departure function α_{ij}^r is available, F_{ij} is equal to zero. The functional form of the departure term $\alpha_{ij}^r(\tau, \delta)$ consists of polynomial, exponential, and modified Gaussian bell-shaped terms, which were recently introduced by Bell *et al.*,¹⁰

$$\alpha_{ij}^{r}(\tau, \delta) = \sum_{k=1}^{K_{\text{pol}ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{\substack{k=K_{\text{pol},ij}+K_{\exp,ij} \\ k_{\text{pol},ij}+K_{\exp,ij}+K_{\text{GBS},ij}}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp(-\delta^{l_{ij,k}}) + \sum_{\substack{k=K_{pol,ij}+K_{\exp,ij}+1 \\ k_{\exp,ij}+K_{\exp,ij}+1}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}}} \times \exp\left[-\eta_{ij,k} \left(\delta - \varepsilon_{ij,k}\right)^2 - \beta_{ij,k} \left(\tau - \gamma_{ij,k}\right)^2\right].$$
(10)

Depending on the desired accuracy and the quantity of the available experimental data, the number of terms used in this work varies between 4 and 8 for the investigated mixtures. The detailed mathematical structure of the departure function for each binary mixture including all parameters is given in Sec. 3.

2.2. Optimization algorithm

For the optimization of $n_{ij,k}$, $d_{ij,k}$, $t_{ij,k}$, $l_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ from Eq. (10) and of the reducing parameters $\beta_{T,ij}$, $\beta_{v,ij}$, $\gamma_{T,ij}$, and $\gamma_{v,ij}$ in Eqs. (6) and (7), a non-linear fitting algorithm developed by Lemmon and Jacobsen¹¹ was used. It iteratively adjusts all parameters to minimize the deviation between the equation of state and selected experimental data points or defined constraints. Depending on the experimental uncertainty, selected data are individually weighted and thus considered differently by the algorithm. The relative deviation F_x between an experimental data point and the value calculated from the equation is defined as

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25 20 $p_{\rm vap,2}$ 15 p / MPaevaluated state point 10 $p_{\rm vap.}$ 5 0.0 0.2 0.40.6 0.81.0 $x_{\rm H}$ - sat. liquid critical point - sat. vapor

FIG. 1. p, x-diagram showing the phase boundary of the binary system CH_4 + H_2 at 153 K.

$$F_x = \frac{\Delta X}{X} = \frac{x_{\text{DATA}} - x_{\text{EOS}}}{x_{\text{DATA}}}.$$
(11)

In addition to the adjustment to experimental data, the fitting algorithm allows for the application of constraints. Constraints were used to define limiting values for parameters and to control the physical behavior of thermodynamic properties in regions that are not covered by experimental data. For the visual evaluation of different properties and derivatives over a wide temperature, pressure, and composition range, thermodynamic software tools, such as REFPROP,¹² TREND,¹³ or CoolProp,¹⁴ can be used. Based on the weighted data points and defined constraints, the fitting algorithm optimizes the equation parameters simultaneously.

For the statistical analyses of the database, the relative deviation of each data point was evaluated according to Eq. (11). The average absolute relative deviation (AARD) of each dataset is described by

AARD =
$$\frac{100}{N} \sum_{i=1}^{N} |F_{x,i}|.$$
 (12)

Since the AARD is not meaningful in certain cases or gives misleading indications, the evaluation of some properties, e.g., the virial coefficients, is carried out in terms of the average absolute deviation,

TABLE 2. Binary-specific reducing parameters; cf. Eqs. (6) and (7). $F_{ij} = 1$ for all binary mixtures

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<i>i</i> + <i>j</i>	$\beta_{T,ij}$	$\gamma_{T,ij}$	$\beta_{v,ij}$	γ _{v,ij}
$CH_4 + H_2$	1.033	1.335	1.001	1.075
$N_2 + H_2$	1.022	1.250	0.986	0.783
$CO + H_2$	1.078	1.105	1.037	1.040
$CO_2 + H_2$	0.964	2.014	1.200	0.825

$$AAD = \frac{1}{N} \sum_{i=1}^{N} |\Delta X_i|.$$
(13)

The AAD of vapor-liquid equilibrium (VLE) datasets is subdivided into bubble- and dew-point data. As exemplified in Fig. 1, two different solutions ($p_{vap,1}$ and $p_{vap,2}$) exist for the calculation of a pressure deviation between the model and dew-point data with a higher composition of hydrogen than the composition at the critical point. Furthermore, deviations in terms of the saturated pressure become very high for steep phase boundaries, even though the data points are located near the saturation line. Therefore, deviations between values calculated with the model and VLE data points are calculated with respect to their mole fractions. Consequently, the deviation cannot be calculated for data points at pressures above the critical pressure according to the model. Those data points were not considered in the calculation of the AAD. The number of calculated data points is given for each dataset in Tables 4–11 in Secs. 3.1–3.4.

3. Results for Binary Mixtures

 (MD_{α})

As explained in Sec. 2, Helmholtz energy mixture models depend on the pure-fluid equations of the components. Accordingly, the binaryspecific mixture models presented in this work were adjusted with a specific set of pure-fluid equations. Since the developed equations are intended to improve the description of hydrogen-rich multicomponent mixtures in combination with the GERG-2008 model,⁴ the pure-fluid equations of GERG-2008⁴ were used for methane, nitrogen, carbon monoxide, and carbon dioxide. The pure-fluid equation for hydrogen was replaced by the current reference equation by Leachman *et al.*¹⁵ for the best possible description of hydrogen. The critical properties and molar masses are listed in Table 1.

 $a (ma a 1 dma^{-3})$

TABLE 1.	Molar	mass a	and critical	parameters	s of the	pure-fluid equations	
	ъ	c		14	1-1		

	Reference	M (g mor)	$I_{\rm c}({\rm K})$	$p_{\rm c}$ (MPa)	$p_{\rm c}$ (mor and)
CH_4	5	16.042 46	190.564	4.5992	10.139 342 719 ^a
N_2	5	28.0134	126.192	3.3958	11.1839
CO	16	28.010 1	132.86	3.4982	10.85
CO_2	5	44.009 5	304.1282	7.3773	10.624978698^{a}
H ₂	15	2.015 88	33.145	1.2965	15.508

^aThe number of digits is not related to the accuracy of the property. The publication provides specific values, which are converted to molar values for consistency purposes. For the correct reproduction of the datasets, fewer digits are sufficient. To reproduce the test values from Table 12, all digits have to be used.

k	n _{ij,k}	$t_{ij,k}$	$d_{ij,k}$	$l_{ij,k}$	$\eta_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$	$\varepsilon_{ij,k}$		
				CH_4	+ H ₂					
1	1.690	0.269	1							
2	-1.240	0.410	2							
3	4.630	1.550	1	1						
4	2.900	2.120	2	1						
5	-3.620	0.039	1		0.2080	0.640	1.224	1.59		
6	5.613	0.320	2		0.0327	0.369	1.603	0.13		
7	-1.040	0.414	3		0.0770	0.359	1.655	1.70		
8	-8.670	0.774	1		0.1540	0.374	2.270	0.08		
	$N_2 + H_2$									
1	-1.812	0.924	1	1						
2	-0.612	0.411	2	1						
3	-0.485	2.846	1	2						
4	0.157	3.565	2	2						
5	2.762	3.186	1		1.83	1.08	1.37	2.50		
6	5.195	0.748	1		0.07	0.31	0.89	1.45		
7	-3.751	2.532	1		1.82	1.14	1.55	2.50		
8	-5.506	1.114	1		0.17	0.21	0.21	1.55		
				CO ·	+ H ₂					
1	-0.521	2.250	1							
2	-0.387	0.473	2							
3	-2.590	0.585	1		0.647	0.751	1.86	1.380		
4	4.350	0.091	2		0.344	0.660	2.23	0.773		
				CO_2	+ H ₂					
1	3.56	1.40	1							
2	-0.97	1.12	2							
3	-4.56	1.87	1		0.575	0.510	0.22	0.52		
4	12.12	0.25	2		0.210	0.826	2.12	0.15		
5	-2.43	1.53	3		0.295	0.410	1.44	0.23		
6	-3.17	2.28	1		0.135	1	1.70	0.14		

TABLE 3. Binary-specific parameters of the departure functions; cf. Eq. (10)

The parameters of the reducing functions according to Eqs. (6) and (7) are given in Table 2 for each binary subsystem. The parameters of the departure functions are summarized in Table 3.

Applying other pure-fluid equations leads to slightly different mixture parameters. Since the pure-fluid equations of the GERG-2008⁴ model are not the most accurate ones, mixture models were also developed for the current reference equations. The mathematical structure is identical to the models for the pure-fluid equations from GERG-2008,⁴ but the parameters are slightly different. The results of this adjustment including all parameters, information on the pure fluids, and statistical analysis of the database are given in the supplementary material.

3.1. Methane + hydrogen (CH₄ + H₂)

In the following, the reproduction of available data for the methane-hydrogen system will be discussed. This system is the only binary hydrogen mixture already described with a departure function in the GERG-2008 model.⁴ The departure function presented in this work is mainly based on VLE and density data (see Tables 4 and 5). The most comprehensive VLE dataset for the investigated system was published by Tsang *et al.*¹⁷ The authors measured ten different

isotherms between 92 K and 180 K with pressures up to 138 MPa in a vapor-recirculating equilibrium apparatus, which is described in more detail in Ref. 18. The error in temperature measurement in the liquid-nitrogen-cooled cryostat is specified as 0.02 K, while the pressure uncertainty is 0.5% of the measured values. The combined uncertainty in composition is given as 0.5 mol% and 2 mol% in the critical region due to errors in sampling. Selected isotherms of the dataset are shown in a p, x-diagram in Fig. 2 together with the phase boundaries calculated with the new model and with GERG-2008.

The new model reproduces the saturated liquid data with an AAD_x of 0.97 mol %, whereas the saturated vapor data are reproduced with an AAD_y of 1.7 mol %. The higher AAD of the saturated vapor data is caused by the data at higher equilibrium temperatures. As illustrated in Fig. 2, the deviation in terms of composition of the saturated vapor points between the maximum hydrogen composition and the critical point is greater for higher temperatures than for lower temperatures. However, compared to the GERG-2008⁴ model ($AAD_x = 6.7 \text{ mol }\%$, $AAD_y = 8.2 \text{ mol }\%$), the data reproduction is significantly improved over the entire phase-equilibrium region. The most significant improvements were achieved for temperatures below 120 K. While the GERG-2008⁴ model predicts an open phase boundary for this region, the new model shows good agreement with the experimentally determined closed phase envelopes.

Another comprehensive dataset was provided by Hong and Kobayashi.²⁴ None of the 145 data points were used for fitting, but they confirm the results of Tsang *et al.*¹⁷ Similar to the apparatus of Tsang et al.,¹⁷ the authors used a liquid-nitrogen-cooled VLE cryostat. The uncertainty in temperature and pressure is reported to be 0.01 K and 0.1%, respectively. The apparatus was limited to pressures of 28.5 MPa, so they were unable to measure the full phase boundary at lower temperatures. For mixture preparation, they used hydrogen with a purity of 99.995% and methane with a purity of 99.999%. The maximum analytical error of the chromatographically measured equilibrium composition is given by the authors as 8.3% of the amount of hydrogen at the lowest hydrogen concentration, which corresponds to 0.05 mol% for the liquid phase and 0.28 mol% for the vapor phase. However, neither the GERG-2008 model⁴ nor the new EOS can reproduce the data within the specified uncertainty even though the AAD is reduced from 2.5 mol % to 1.2 mol % for the saturated liquid phase and from 4.0 mol % to 2.1 mol % for the saturated vapor phase with the new EOS in comparison to GERG-2008. Deviations in terms of percentage mole fraction of all available VLE datasets, subdivided into bubble- and dew-point data, are shown in Fig. 3. Data points outside the visible range are displayed at the upper or lower limit of the diagram. This holds for all deviation plots in this article.

Since all properties of a Helmholtz energy model are calculated by combining different derivatives of a single mathematical function, ^{4,54} the adjustment of a single property and the associated change in derivatives also shifts the description of other properties. Figure 4 shows the shifted phase boundary of the binary system $CH_4 + H_2$, which resulted from fitting VLE data, in pressure-temperature diagrams for three different hydrogen compositions. Near the two-phase region, which was calculated with the new EOS, the shift of the phase boundary also affects, e.g., the homogeneous density. Significant density deviations between data calculated from GERG-2008⁴ and from the new model are visible at temperatures below 200 K. The deviations increase with increasing pressure.

TABLE 4. AADs (in mol %) of VLE data calculated with the new model and with GERG-2008⁴ for the binary system $CH_4 + H_2$. *N* indicates the number of available state points of each publication including pure-fluid data. Both AADs and number of data points are listed for bubble-point data (subscript "x") and dew-point data (subscript "y"). The number of calculated points refers to the new EOS. Pure-fluid data as well as data where deviations in terms of mole fraction could not be calculated were not considered for the AADs

	Ava	ilable	data	Calcu	ılated			This	work	GERG	-2008
Author	Ν	N_x	N_y	$N_{x, calc}$	$N_{y, calc}$	$T_{\min} - T_{\max}$ (K)	$p_{\min}-p_{\max}$ (MPa)	$\overline{AAD_x}$	AAD_y	AAD_x	AAD_y
Augood (1957) ¹⁹	3	3	2	3	2	111.71	2.3-18.1	0.99	0.86	0.56	1.3
Benham and Katz (1957) ²⁰	13	13	13	13	13	116-173	3.3-27.6	1.5	1.9	2.1	3.2
Cosway and Katz (1959) ²¹	3	3	3	2	2	144-200	3.4-6.9	0.39	3.8	0.20	4.6
Fastovskii and Gonikberg (1940) ²²	35	34	32	34	32	90-127	3.1-23.0	1.0	2.3	0.81	2.6
Freeth and Verschoyle (1931) ²³	21	15	20	15	20	90-91	1.7-20.9	1.0	0.48	1.2	0.56
Hong and Kobayashi (1981) ²⁴	145	130	135	130	135	108-184	< 0.1-28.5	1.2	2.1	2.5	4.0
Hong and Kobayashi (1981) ²⁵	28	28	28	28	28	108-174	2.7 - 10.4	0.48	0.66	0.45	1.5
Hu <i>et al.</i> $(2014)^{26}$	23	23	23	23	23	100-121	0.2-2.3	0.15	5.2	0.042	5.1
Kirk and Ziegler (1965) ²⁷	38	0	38	0	38	89-117	1.0-12.7		0.076		0.062
Kremer and Knapp (1983) ²⁸	3	3	3	3	3	140-145	2.8-5.0	0.48	0.65	0.17	1.3
Levitskaya (1941) ²⁹	9	9	9	8	8	158-189	3.0-8.2	0.73	2.5	0.74	1.8
Likhter and Tikhonovich (1940) ³⁰	53	24	25	23	24	158-189	1.5-8.4	0.89	3.5	1.0	3.6
Sagara <i>et al.</i> $(1972)^{31}$	28	28	28	28	28	103-174	1.0-10.9	0.81	2.2	1.0	3.7
Tsang <i>et al.</i> $(1980)^{17}$	196	190	190	188	188	92-181	0.2-138.0	0.97	1.7	6.7	8.2
Yorizane <i>et al.</i> $(1980)^{32}$	3	3	3	3	3	93.61	10.1-15.2	1.3	0.29	1.2	0.43
Yorizane <i>et al.</i> $(1968)^{33}$	25	23	25	23	25	103–164	1.0–15.2	1.2	2.8	1.3	3.4

TABLE 5. AARDs and AADs of homogeneous data calculated with the new model and with GERG-2008⁺ for the binary system CH₄ + H₂. The corresponding unit of each AAD is given after the respective property. *N* indicates the number of available state points of each publication including pure-fluid data. Pure-fluid data are not considered in the calculation of the overall AARD/AAD

Author	N	$T_{\min} - T_{\max}$ (K)	$p_{\min}-p_{\max}$ (MPa)	$x_{\rm CH_4,min}$ - $x_{\rm CH_4,ma}$	x AARD _{This work}	$AARD_{GERG-2008}$						
Density $p\rho T \bar{x}$												
Chuang <i>et al.</i> $(1976)^{34}$	146	173-274	0.4-50.6	0.21-0.81	1.0	0.9						
Hernández-Gómez et al. (2018) ³⁵	391	240-350	1.0-19.9	0.50-0.95	0.048	0.052						
Iwasaki and Takahashi (1961) ³⁶	63	298-349	0.1-31.2	0.36-0.81	0.99	0.98						
Jaeschke and Humphreys (1990) ³⁷	899	270-354	0.2-30.5	0.25-0.85	0.019	0.018						
Jett (1990) ³⁸	276	135-274	<0.1-69.9	0.9535	0.60	0.58						
Jett <i>et al.</i> $(1994)^{39}$	9	142-189	2.2-5.5	0.9535	1.2	1.4						
Kritschewsky and Levchenko (1941) ⁴⁰	70	273-474	10.1-70.9	0.33-0.86	0.45	0.46						
Machado <i>et al.</i> $(1988)^{41}$	296	130-160	1.7-107	0.09-0.92	1.0	0.95						
Magee <i>et al.</i> $(1985)^{42}$	160	273-601	0.3-71.5	0.7995	0.27	0.26						
Magee and Kobayashi (1986) ⁴³	165	160-274	1.8-69.7	0.7995	0.96	1.0						
Mihara <i>et al.</i> (1977) ⁴⁴	153	298-349	0.3-9.2	0.32-0.78	0.14	0.15						
Solbrig and Ellington (1963) ⁴⁵	98	138-423	1.2-22.8	0.0903	0.18	0.19						
Vilcu et al. (1977) ⁴⁶	6	298.15	1.0-6.1	0.52-0.63	2.6	2.6						
		Spee	ed of sound w									
Lozano-Martin <i>et al.</i> (2020) ⁴⁷	232	273-375	0.4-20.2	0.50-0.95	0.030	0.036						
Maurer (2021) ⁴⁸	135	249-350	0.5-10.1	0.9537	0.028	0.033						
Author	Ν	$T_{\min} - T_{\max}$ (K	$x_{CH_4,min}$	$-x_{\rm CH_4,max}$	AAD _{This work}	AAD _{GERG-2008}						
		Second virial co	pefficient B^{a} (cm ³ r	nol^{-1})								
Brewer (1967) ⁴⁹	1	273.15	•	••	0.61	0.016						
Brewer (1967) ⁴⁹	1	273.15			0.69 ^b	0.068 ^b						
Magee (1983) ⁵²	49	190-500	0.7	995	0.74 ^c	0.87 ^c						
Mason and Eakin (1961) ⁵³	2	288.7	0.49	-0.51	4.5	4.9						
Mihara <i>et al.</i> (1977) ⁴⁴	20	298-349	0.32	-0.78	1.7 ^c	2.1 ^c						
Solbrig and Ellington (1963) ⁴⁵	12	138-423	0.0	903	2.0	1.8						

^aIf no composition range is given, the dataset contains only the composition-independent B₁₂ and no composition-dependent B.

^bThe composition-independent B₁₂ was corrected according to the method given by Garberoglio *et al.*⁵⁰ and the current reference pure-fluid equations.^{15,51}

^cDataset also contains the composition-independent B_{12} .



FIG. 2. p, x-diagram showing VLE data at 110 K, 140 K, and 170 K for the binary system CH₄ + H₂.

In addition to the adjusted phase boundary, the homogeneous region is also influenced by simultaneously fitted density data. Overall, 13 different datasets for the homogeneous density are available in the literature. Deviations are summarized in Table 5. The main dataset considered in the fitting process was measured by Jaeschke and Humphreys.³⁷ It was part of a comprehensive research program to determine natural-gas properties and, therefore, also an important dataset for the development of the GERG-2008.⁴ For determining the homogeneous density in a temperature range between 270 K and 354 K with pressures up to 30.5 MPa and a composition range from 15 mol % to 75 mol % hydrogen, the authors measured the compressibility factor with a Burnett apparatus and the refractive index with an optical interferometry apparatus. The expanded uncertainty (k = 2) is estimated to be 0.07%-0.08% in density. Both models reproduce the 899 data points with an AARD of 0.019% and, thus, well within their experimental uncertainty. For temperatures below 270 K, a few data points of Hernández-Gómez et al.³⁵ were used in the fitting process. The recently published data were measured with a single-sinker densimeter with a magnetic suspension coupling



FIG. 3. Deviation of bubble-point data (top) and dew-point data (bottom) from values calculated with the new EOS (left) and GERG-2008⁴ (right) for the binary system CH₄ + H₂. The ordinate is linearly scaled between the dashed lines and logarithmically scaled in the gray filled regions.



FIG. 4. Percentage deviation in density in the homogeneous region between the new EOS and GERG-2008⁴ for the binary system CH₄ + H₂. The white dashed lines represent the normal range of validity of both models, and the black dashed lines mark the phase boundary calculated with GERG-2008. The upper temperature and pressure limits of both axes are based on the extended range of validity for both models. The gray filled area is the two-phase region calculated with the new EOS.

and show very good agreement with the data of Jaeschke and Humphreys³⁷ in their common temperature, pressure, and composition range. Consequently, they extend the range of reliable data to

lower temperatures (240 K) and lower hydrogen fractions (5 mol %). Again, the new EOS and the GERG-2008 model show similar performance and reproduce the 391 data points with an AARD of 0.048%



FIG. 5. Percentage deviation of homogeneous density data from the new EOS (left) and GERG-2008⁴ (right) for the binary system CH₄ + H₂. The ordinate is linearly scaled between the dashed lines and logarithmically scaled in the gray filled regions.



FIG. 6. Percentage deviation of speed of sound data from the new EOS (top) and GERG-2008⁴ (bottom) for the binary system $CH_4 + H_2$.

and 0.052%, respectively, which is within the specified experimental expanded uncertainty (k = 2) of ~0.09%.

For modeling the even lower temperature and higher pressure region, some data points of Machado *et al.*⁴¹ were selected. However, these points were only considered with low weights since higher weights led to higher deviations of the datasets discussed before. The reported overall experimental uncertainty of 0.2% stated by Machado *et al.*⁴¹ cannot be achieved by any of the models (AARD_{This work} = 1.0% and AARD_{GERG-2008} = 0.95%). However, since these data are the only available data for pressures up to 107 MPa, they were still used for fitting the equation. At temperatures higher than 354 K, the new EOS was adjusted to data of Solbrig and Ellington,⁴⁵ who measured compressibility factors of

hydrogen-rich (90 mol%) mixtures at temperatures up to 423 K. The estimated overall experimental uncertainty of 0.1% cannot be reached by either model. However, due to the scattering of the data points, the claimed uncertainty seems questionable. An overview of the performance of the new model and GERG-2008⁴ in reproducing all available density data is given in Fig. 5.

In addition to the phase equilibrium and homogeneous density data, two speed of sound and five thermal virial coefficient datasets are available; cf. Table 5. Although neither of the two models was fitted to the data of Lazano-Martin *et al.*⁴⁷ or Maurer,⁴⁸ they reproduce all data with almost identical deviations (see Fig. 6).

3.2. Nitrogen + hydrogen (N₂ + H₂)

The available database for the binary system nitrogen + hydrogen consists mainly of VLE and density data and is, therefore, comparable with the database for methane + hydrogen. Summaries of the available data are given in Tables 6 and 7. The GERG-2008⁴ model describes the nitrogen + hydrogen system with adjusted reducing parameters but without a departure function. The EOS presented here includes a departure function, through which the phase boundary can be described more accurately. For modeling the phase envelopes, the dataset of Streett and Calado¹⁸ was used, which is comprised of seven isotherms in a temperature range between 63 K and 110 K with pressures up to 57.2 MPa. Selected isotherms of the dataset are shown in a *p*, *x*-diagram in Fig. 7 together with the phase boundaries calculated with the presented model and GERG-2008.

The experimental setup is the same as that of Tsang *et al.*¹⁷ used for their methane + hydrogen measurements, although the experimental uncertainty is estimated to be lower. The stated measurement uncertainties are 0.1 K in terms of temperature, 0.05 MPa in terms of pressure, and 0.1 mol % or less in gas analysis. However, we conclude that the uncertainties were estimated too optimistically; in particular,

TABLE 6. AADs (in mol %) of VLE data calculated with the new model and with GERG-2008⁺ for the binary system N₂ + H₂. *N* indicates the number of available state points of each publication including pure-fluid data. Both AADs and number of data points are listed for bubble-point data (subscript "x") and dew-point data (subscript "y"). The number of calculated points refers to the new EOS. Pure-fluid data as well as data where deviations in terms of mole fraction could not be calculated were not considered for the AADs

	Ava	ilable	data	Calcı	ılated			This	work	GERG	G-2008
Author	Ν	N_x	N_y	$N_{x,calc}$	$N_{y,calc}$	$T_{\min} - T_{\max}$ (K)	p_{\min} - p_{\max} (MPa)	AAD_x	AAD_y	AAD_x	AAD_y
Akers and Eubanks (1960) ⁵⁸	10	10	10	10	10	83-123	2.2-13.8	0.39	1.1	7.6	3.1
Augood (1957) ¹⁹	10	10	7	10	7	67-78	2.7-17.9	6.7	4.1	19	2.2
Eubanks (1957) ⁵⁹	15	15	15	14	14	83-123	2.2-15.9	0.97	0.93	11	5.2
Gonikberg <i>et al.</i> (1939) ⁵⁵	40	38	35	34	31	78-110	0.1-17.8	2.1	3.1	15	8.2
Knapp <i>et al.</i> (1976) ⁶⁰	5	0	5	0	4	90-124	3.0		1.6		4.6
Kremer and Knapp (1983) ²⁸	3	3	3	3	3	80.01	5.0-10.0	0.24	0.55	9.7	1.7
Maimoni $(1961)^{\overline{61}}$	17	13	17	11	15	90-96	0.4-4.6	0.091	0.22	2.2	1.5
Omar and Dokoupil (1962) ⁶²	34	10	34	10	34	63-76	0.1-7.1	0.29	0.47	2.6	0.73
Steckel and Zinn (1939) ⁶³	14	14	14	11	11	107-114	2.5-9.2	1.2	1.8	8.4	11
Streett and Calado (1978) ¹⁸	77	76	74	76	74	63-111	1.0-57.2	1.3	1.4	21	18
Verschoyle (1931) ⁶⁴	89	65	77	61	76	57-89	0.1-22.8	1.5	1.7	15	3.5
Xiao and Liu (1990) ⁶⁵	16	16	16	16	16	100	1.4-4.6	0.15	0.58	2.5	2.1
Yorizane (1971) ⁵⁶	17	17	17	17	17	77-89	1.7-19.0	2.3	1.6	18	5.3
Yorizane <i>et al.</i> (1968) ³³	12	11	12	11	12	77.36	0.5–15.2	1.9	1.1	13	3.3

TABLE 7. AARDs and AADs of homogeneous data calculated with the new model and with GERG-2008¹ for the binary system $N_2 + H_2$. The corresponding unit of each AAD is given after the respective property. *N* indicates the number of available state points of each publication including pure-fluid data. Pure-fluid data are not considered in the calculation of the overall AARD/AAD

Author	Ν	$T_{\min} - T_{\max}$ (K)	p_{\min} - p_{\max} (MPa)	$x_{N_2,min}-x_{N_2,ma}$	ax AARD _{This work}	AARD _{GERG-2008}
		Dens	sity $p\rho T \bar{x}$			
Bartlett et al. $(1928)^{66}$	47	273-573	5.1-102	0.25	0.19	0.21
Bennett and Dodge (1952) ⁶⁷	77	298-399	99.9-308	0.25-0.75	0.22	0.75
Deming and Shupe (1931) ⁶⁸	93	203-574	3.4-149	0.25	0.20	0.32
Jaeschke et al. (1991) ⁶⁹	1002	270-354	0.3-30.2	0.25-0.85	0.026	0.025
Kritschewsky and Markov (1940) ⁷⁰	30	273-474	5.1-50.7	0.93-0.94	1.5	1.5
Lialine <i>et al.</i> $(1957)^{71}$	108	322-446	1.5-157	0.92 - 0.94	2.3	2.3
Mastinu (1967) ⁵⁷	10	77.41	1.2	0.98-0.99	0.41	2.5
Michels and Wassenaar (1949) ⁷²	119	273-424	1.9-33.8	0.248	0.026	0.014
Sage <i>et al.</i> (1948) ⁷³	90	277-511	0.1-104	0.24	0.11	0.14
Verschoyle (1926) ⁷⁴	63	273-294	3.7-20.8	0.25-0.75	0.077	0.095
Wiebe and Gaddy (1938) ⁷⁵	175	273-574	2.5-102	0.13-0.74	0.13	0.18
Zandbergen and Beenakker (1967) ⁷⁶	104	170-293	0.3-10.0	0.26-0.80	0.65	0.85
-		Speed	of sound w			
van Itterbeek and van Doninck (1944) ⁷⁷	29	90.22	< 0.1	0.45 - 0.80	0.31	0.32
van Itterbeek and van Doninck (1949) ⁷⁸	27	75–91	<0.1	0.00 - 1.00	0.34	0.34
Author	Ν	$T_{\min} - T_{\max}$ (K	$x_{N_2,min}$	$x_{N_2,max}$	AAD _{This work}	AAD _{GERG-2008}
		Second virial coef	fficient B^{a} (cm ³ mol	l^{-1})		
Brewer and Vaughn (1969) ⁴⁹	8	123-324			0.69	2.5
Brewer and Vaughn (1969) ⁴⁹	8	123-324			0.87^{b}	2.1 ^b
Edwards and Roseveare (1942) ⁸⁰	1	298.14			0.95	1.4
Jaeschke <i>et al.</i> (1991) ⁶⁹	27	270-354	0.25-	0.85	0.33 ^c	0.10 ^c
Michels and Wassenaar (1949) ⁷²	7	273-424			3.9	4.3

^aIf no composition range is given, the dataset contains only the composition-independent B_{12} and no composition-dependent B.

^bThe composition-independent B₁₂ was corrected according to the method given by Garberoglio et al.⁵⁰ and the current reference pure-fluid equations.^{15,79}

^cDataset also contains the composition-independent B_{12} .

the saturated vapor data points at temperatures below 80 K show slight inconsistencies (see data in Fig. 8 highlighted in red). While the presented EOS shows good agreement with the experimentally determined phase boundary over the entire temperature, pressure, and composition range, the GERG-2008 model deviates systematically with increasing pressure and decreasing temperature. The maximum deviation occurs near the critical point. The critical pressure is overestimated by GERG-2008 by at least a factor of 2. For temperatures below 100 K, the GERG-2008 model even predicts an open phase boundary, which is contradictory to the experimental data.^{55,56} Consequently, the representation of all available VLE datasets is improved with the new EOS. This is shown in Fig. 9 and Table 6.

As already mentioned in Sec. 3.1, the shifted phase boundary has a significant impact on the homogeneous region. In Fig. 10, percentage deviations between the new EOS and the GERG-2008 model⁴ in density in the homogeneous region are shown in *p*, *T*diagrams for three different hydrogen mole fractions. The highest deviations occur where the slope and curvature of the phase boundary has changed the most. This is particularly relevant as this region is within the normal range of validity of both models. However, this difference is caused by the shift of the phase boundary as no homogeneous data in the temperature region below 200 K were used for developing the new EOS. Only Mastinu⁵⁷ provided ten data points at 1.2 MPa with a low hydrogen concentration with a maximum of 2 mol % in the temperature range where the two-phase region is present. Although none of these data points were used for adjusting the new EOS, the AARD of the new model is lower (AARD = 0.41%) than the AARD of the GERG-2008 model (AARD = 2.5%). Even if the dataset covers only a very small region, the lower AARD and the better reproduction of the phase-equilibrium data indicate that the region near the phase boundary is more accurately described with the new EOS. However, without additional accurate measurements, this advantage can hardly be quantified.

At temperatures from 270 K to 354 K, the new EOS is based on the dataset of Jaeschke *et al.*⁶⁹ Similar to their density measurements for the methane-hydrogen system,³⁷ the authors used a Burnett apparatus and a grating interferometer to determine the compressibility of four different nitrogen-hydrogen mixtures with a maximum hydrogen composition of 75 mol %. Due to the high consistency of the 1002 data points and the low reported overall experimental uncertainty of 0.07% for pressures below 10 MPa and 0.1% for pressures up to 30.2 MPa, this dataset was favored. Furthermore, their results are confirmed by the highly accurate data from Michels and Wassenaar.⁷² Since both datasets correspond very well in their common region and Michels and Wassenaar⁷² additionally measured higher–temperature isotherms than Jaeschke *et al.*,⁶⁹ the data of Michels and Wassenaar⁷²



FIG. 7. p, x-diagram showing VLE data at 70.4 K, 90.8 K, and 110.3 K for the binary system N₂ + H₂.

were used for fitting the homogeneous density at temperatures up to $424\,$ K.

Both models perform almost identically in this region and reproduce the two datasets with very low AARDs (see Table 7).

For the temperature region from 424 K to 511 K and pressures up to 104 MPa, a few data points of Sage et al.⁷³ were fitted with low weights. Figure 11 shows that the deviations between this dataset and the new model increase with increasing pressure, which is in line with the experimental uncertainty of 0.2% for the low-pressure and 0.4% for the high-pressure range. At pressures higher than 100 MPa, the present EOS was fitted to the data of Bennett and Dodge.⁶⁷ The authors measured compressibility factors with the Burnett method with an estimated uncertainty of 0.37%. This dataset includes two outliers, which differ significantly from the other data points and were, therefore, not included in the AARD. The new EOS reproduces most of the data within the specified uncertainty with an overall AARD of 0.22%, whereas the GERG-2008 model⁴ reproduces them with an AARD of 0.75%. Furthermore, a distinct increase in deviation is apparent in the high-pressure and low-temperature region for GERG-2008.

Beside the VLE and density data, two speed of sound and five virial coefficient datasets are available for the binary system nitrogen



FIG. 8. p, x-diagram showing VLE data at 77.6 K for the binary system N₂ + H₂. Scattered data of the isotherm are highlighted in red.

+ hydrogen. Both speed of sound datasets were measured by van Itterbeek and van Doninck.^{77,78} Since the authors do not provide a detailed uncertainty analysis and the data are represented well both by GERG-2008 and the new model, they were used solely for validation. The same applies to the representation of the virial coefficients since most were determined from density data, which were directly used to adjust the homogeneous density.

3.3. Carbon monoxide + hydrogen (CO + H₂)

The available database for the system carbon monoxide + hydrogen is more restricted than for methane + hydrogen and nitrogen + hydrogen. Although VLE and density data are available for this system, most publications are less comprehensive and the number of data is more limited. An overview of the available data is given in Tables 8 and 9. For the phase boundary, seven VLE datasets are available. The most comprehensive one is provided by Tsang and Streett⁸¹ and contains 134 data points in a temperature range from 70 K to 126 K with pressures up to 53 MPa. Like the dataset for methane + hydrogen by Tsang *et al.*¹⁷ and the dataset for nitrogen + hydrogen by Streett and Calado,¹⁸ these data were measured as part of a research program to determine the phase behavior of binary hydrogen mixtures in the 1980s. Consequently, the experimental setup and method are identical to Streett and Calado.¹⁸ The temperature is estimated to be accurate within 0.02 K and pressures to be accurate within 0.5% of the measured value. The uncertainty in composition is given as 0.5 mol % and 2 mol % in the critical region. Selected isotherms of the dataset are shown in a p, x-diagram in Fig. 12 together with the phase boundaries calculated with the new model and with GERG-2008.⁴ The present EOS matches the experimental data very well over the entire temperature, pressure, and composition range. It reproduces the bubble-point data with an AAD of 0.89 mol % and the dew-point data with an AAD of 0.95 mol %. GERG-2008, on the other hand, matches the data only at high temperatures and low pressures. With decreasing temperature and increasing pressure, the shift between the model and the experimental data becomes more distinct. For temperatures below 80 K, the GERG-2008 model predicts an open phase envelope, which contradicts the experimental data. A dataset that shows good agreement with the results of Tsang and Streett⁸¹ is the dataset of Verschoyle.⁶⁴ However, the author measured fewer points in a more limited state region with a volumetric method. The uncertainty in temperature is given as 0.02 K and the uncertainty in pressure is given as 0.005 MPa, which seems optimistic even in comparison to modern measuring instruments. For the uncertainty in composition, different error sources are discussed in the publication, but no overall uncertainty is specified. The other available datasets contain significantly fewer data points and do not extend the temperature and pressure range of Tsang and Streett.⁸¹ Deviations in terms of percentage mole fraction of all available VLE datasets, subdivided into bubble- and dew-point data, are shown in Fig. 13 and are listed in Table 8.

Similar to the binary systems methane + hydrogen and nitrogen + hydrogen, the changed phase boundary has a remarkable impact on the homogeneous region (see Fig. 14). Since the curvature and slope of the phase boundary were significantly modified in certain regions, the homogeneous region near the two-phase region is strongly influenced. The highest deviation of up to 10% in terms of density between values calculated from GERG-2008⁴ and from the





new model within the normal range of validity is found at the equimolar composition and temperatures below 200 K. At higher pressures, deviations on the order of 10% are also observed for higher temperatures. Both at higher and lower hydrogen concentrations, the deviations decrease slightly.

For fitting the homogeneous region, only three different density datasets are available in the literature for carbon monoxide + hydrogen. The most recently published dataset by Cipollina *et al.*⁸³ deviates more than 70% both from values calculated with the new EOS and GERG-2008.⁴ We assumed that the high deviations are due to an



FIG. 10. Percentage deviation in density in the homogeneous region between the new EOS and GERG-2008⁴ for the binary system $N_2 + H_2$. The white dashed lines represent the normal range of validity of both models, and the black dashed lines mark the phase boundary calculated with GERG-2008. The upper temperature and pressure limits of both axes are based on the extended range of validity for both models. The gray filled area is the two-phase region calculated with the new EOS.



FIG. 11. Percentage deviation of homogeneous density data from the new EOS (left) and GERG-2008⁺ (right) for the binary system N₂ + H₂. The ordinate is linearly scaled between the dashed lines and logarithmically scaled in the gray filled regions.

error in the publication since the publication also contains density data for the binary system carbon dioxide + hydrogen that deviate with an AARD of only 2.8% from GERG-2008.⁴ The datasets by Scott⁸⁴ and Townend and Bhatt⁸⁵ were measured by a research group of the Imperial College of Science and Technology in London in the 1930s. The authors do not provide a detailed uncertainty analysis, and we conclude that the data do not fulfill the accuracy requirements for developing an accurate EOS. The indicators for this assumption are, on the one hand, the purity of pure substances used, which was 99.9% for hydrogen and 99.5% for carbon monoxide and, on the other hand, the results obtained during the development of the EOS. The relatively high amount of unknown impurities can have a significant impact on the fluid behavior and, therefore, could be a reason why the data do not fulfill the accuracy requirements. Nevertheless, the dataset of Townend and Bhatt⁸⁵ was favored since the data cover a wider temperature and pressure range. However, even with high weights, it was not possible to reproduce these data with low and consistent deviations without a loss of accuracy in the description of the phase boundary. Consequently, only a few data points were fitted with low weights. The resulting deviations are illustrated in Fig. 15 in comparison to deviations calculated with GERG-2008. Since both datasets consist of only one or two isotherms, the deviations are not shown over temperature.

TABLE 8.	AADs (in mol %) of VLE data calculated with the new model and GERG-2008	for the binary system CO + H ₂ .	N indicates the number of data poin	ts of each publication.
Both AADs	and number of data points are listed for bubble-point data (subscript "x") and de	ew-point data (subscript "y"). The	number of calculated points refers t	to the new EOS. Pure-
fluid data a	as well as data where deviations in terms of mole fraction could not be calcu	lated were not considered for t	he AADs	

		Available data		Calculated				This work		GERG-2008	
Author	Ν	N_x	N_y	$N_{x,calc}$	$N_{y, calc}$	$T_{\min} - T_{\max}$ (K)	p_{\min} - p_{\max} (MPa)	AAD _x	AAD_y	AAD _x	AAD_y
Akers and Eubanks (1960) ⁵⁸	11	11	11	11	11	83-123	2.2-13.8	0.28	0.91	6.6	4.2
Augood (1957) ¹⁹	4	4	4	4	4	81.42	9.5-18.1	1.3	5.0	7.4	20
Eubanks (1957) ⁵⁹	21	21	21	21	21	83-123	2.2-24.1	1.7	1.8	6.6	4.2
Hong and Kobayashi (1981) ²⁴	11	11	11	11	11	108-124	2.8-6.9	0.36	0.78	4.6	1.2
Kremer and Knapp (1983) ²⁸	1	1	1	1	1	120.01	5.0	0.39	0.60	4.7	0.16
Tsang and Streett (1981) ⁸²	134	134	134	134	133	70-126	0.5-52.9	0.89	0.95	8.7	4.4
Verschoyle (1931) ⁶⁴	78	78	78	65	73	67-89	1.7-24.8	1.6	0.88	6.0	4.2
Yorizane <i>et al.</i> (1968) ³³	24	16	23	15	23	77–124	0.6–15.2	1.8	1.7	4.3	2.6

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TABLE 9. AARDs and AADs of homogeneous data calculated with the new model and with GERG-2008⁴ for the binary system CO + H₂. The corresponding unit of each AAD is given after the respective property. *N* indicates the number of available state points of each publication including pure-fluid data. Pure-fluid data are not considered in the calculation of the overall AARD/AAD

Authors	N	$T_{\min} - T_{\max}$ (K)	p_{\min} - p_{\max} (MPa)	$x_{\rm CO,min} - x_{\rm CO,max}$	$AARD_{This \ work}$	AARD _{GERG-2008}			
Density $p\rho T \bar{x}$									
Cipollina <i>et al.</i> $(2007)^{83}$	48	308-343	8.8-23.1	0.89-0.95	74	74			
Scott (1929) ⁸⁴	54	298.14	0.1-17.2	0.34-0.67	0.19	0.18			
Townend and Bhatt (1931) ⁸⁵	114	273-299	1.0-60.8	0.33-0.67	0.17	0.72			
		Speed	l of sound <i>w</i>						
van Itterbeek and van Doninck (194	19) ⁷⁸ 16	75–91	<0.1	0.17-0.88	0.22	0.22			
Authors	Ν	$T_{\min} - T_{\max}$ (K)) $x_{\rm CO,min}$	x _{CO,max} A	AD _{This work}	AAD _{GERG-2008}			
		Second virial coe	efficient B_{12} (cm ³ m	ol ⁻¹)					
Brewer (1967) ⁴⁹	1	273.15			0.77	3.3			
Brewer (1967) ⁴⁹	1	273.15			1.16 ^a	2.9 ^a			
Garberoglio et al. (2017) ⁵⁰	24	80-2000			0.96	4.4			
Reuss and Beenakker (1956) ⁸⁶	7	35-61			18	17			
Schramm <i>et al.</i> (1991) ⁸⁷	5	77–297			7.3	14			

^aThe composition-independent B_{12} was corrected according to the method given by Garberoglio *et al.*⁵⁰ and the current reference pure-fluid equations.^{15,16}

Furthermore, one speed of sound dataset by van Itterbeck and van Doninck⁷⁸ and four datasets for the second mixture virial coefficients are available. None of these data were used to fit the equation but for validation purposes (see Table 9). Garberoglio *et al.*⁵⁰ used an all-dimensional potential and the path-integral method to compute the second virial coefficient in a temperature range between 10 K and 2000 K. However, since the data below the triple-point temperature of CO ($T_{tp,CO} = 68.16$ K)⁸⁸ show a significantly higher deviation, only the data between 80 K and 2000 K were considered for the validation. The authors estimated the uncertainty of each data point based on a comprehensive and detailed analysis. Within the temperature range between 80 K and 2000 K, the average expanded uncertainty (k = 2) is estimated to be 0.66 cm³ mol⁻¹. Even though the new EOS does not reproduce the data



FIG. 12. $\rho,$ x-diagram showing VLE data at 70 K, 95 K, and 125 K for the binary system CO + H_2.

within the estimated uncertainty, the AAD was reduced from $4.4 \text{ cm}^3 \text{ mol}^{-1}$ to 0.96 cm³ mol⁻¹ compared to GERG-2008.⁴

3.4. Carbon dioxide + hydrogen (CO₂ + H₂)

With regard to the quantity of experimental data points, the database for the binary system carbon dioxide + hydrogen is comparable with the databases for methane + hydrogen or nitrogen + hydrogen. Sources of the available data are listed in Tables 10 and 11. The VLE data cover almost the entire temperature region from the triple-point temperature ($T_{\rm tp,CO_2} = 216.59 \text{ K}$)^{89,90} up to the critical temperature ($T_{\rm c,CO_2} = 304.13 \text{ K}$)⁹¹ of pure CO₂.

A highly accurate and comprehensive dataset in this temperature range was provided by Fandiño et al.93 The authors measured nine isotherms with a pressure of up to 15 MPa with a static-analytic method where a gas chromatograph is connected to a VLE cell. Based on a detailed uncertainty analysis, they specified an expanded uncertainty (k = 2) in terms of temperature of 0.01 K and 0.006 MPa in terms of pressure. The expanded uncertainty (k = 2) of the composition depends on the mole fraction and varies between 0.01 mol % and 0.32 mol % for the saturated liquid phase and 0.54 mol % for the saturated vapor phase. The bubble-point data are reproduced with an AAD of 0.15 mol % and the dew-point data with an AAD of 0.55 mol % by the new EOS. Thus, the bubble-point data are well represented within the uncertainty and the AAD of the dew-point data is slightly higher than the uncertainty. However, compared to GERG-2008, which reproduces the data with AADs of 0.55 mol % and 2.6 mol %, the deviations were significantly reduced. Due to the maximum working pressure of 20 MPa of the VLE cell, Fandiño et al.93 were not able to measure the complete phase envelopes at low temperatures. Hence, the dataset of Tsang and Streett⁸² was used for modeling the phase boundary at pressures higher than 15 MPa. Similar to their measurements for methane + hydrogen¹⁷ and carbon monoxide + hydrogen,⁸¹ the authors estimated the accuracy of the temperature at 0.02 K and the accuracy of the pressure at 0.5% of the measured value.



FIG. 13. Deviation of bubble-point data (top) and dew-point data (bottom) from values calculated with the new EOS (left) and GERG-2008⁴ (right) for the binary system CO + H₂. The ordinate is linearly scaled between the dashed lines and logarithmically scaled in the gray filled region.

The uncertainty of the composition is estimated to be 0.5 mol % and 2 mol % in the critical region. As shown in Fig. 16 for selected isotherms, both the data of Tsang and Streett⁸² and the data of Fandiño *et al.*⁹³ are well represented by the new mixture model. The GERG-2008 model overestimates the pressure of the phase envelope at high temperatures. With increasing temperature, the GERG-2008 model shows better agreement with the data at low pressures. However, the deviation between the data and the model increases with increasing

pressure. Furthermore, the GERG-2008 model predicts an open phase boundary for temperatures lower than 260 K, which contradicts the data of Tsang and Streett.⁸² The deviations of all available VLE data from the new EOS and from GERG-2008⁴ are illustrated in Fig. 17 and listed in Table 10.

The different course of the phase boundary between the two models also affects the homogeneous region near the two-phase region, as shown in Fig. 18 for calculated densities. While the



FIG. 14. Percentage deviation in density in the homogeneous region between the new EOS and GERG-2008⁴ for the binary system CO + H₂. The white dashed lines represent the normal range of validity of both models, and the black dashed lines mark the phase boundary calculated with GERG-2008. The upper temperature and pressure limits of both axes are based on the extended range of validity for both models. The gray filled area is the two-phase region calculated with the new EOS.



FIG. 15. Percentage deviation of homogeneous density data from values calculated from the new EOS (top) and GERG-2008⁴ (bottom) for the binary system CO + H_2 . The ordinate is linearly scaled between the dashed lines and logarithmically scaled in the gray filled regions.

percentage deviation is relatively small for high hydrogen concentrations, it increases to over 10% in the extended range of validity for lower concentrations. Within the normal range of validity, the difference is most distinct at temperatures below 350 K and pressures above 20 MPa. Although no highly accurate experimental homogeneous density data are available in this state region for validation, the more accurate representation of the VLE data and the good agreement with homogeneous density data in other regions indicates that the new EOS describes the homogeneous region more accurately.

Overall, 11 homogeneous density datasets are available in the literature that cover temperatures from 253 K to 474 K at pressures up to 49 MPa with hydrogen concentrations between 1 mol % and 86 mol%. The new EOS was mainly fitted to a subset of the 263 data points of Jaeschke and Humphreys,³⁷ which ranges from 274 K to 350 K in temperature and up to 12.6 MPa in pressure. As already discussed for methane + hydrogen, the combined experimental uncertainties (k = 2) are estimated to be within 0.07% and 0.08%. Except for some data points on the 274 K isotherm, the majority of the data are reproduced within the specified uncertainty. As shown in Fig. 19, deviations on the 274 K isotherm increase slightly at increasing pressures. This increase is also apparent for values calculated from GERG-2008 and could not be completely eliminated in the new EOS. Nevertheless, the data are very consistent and are, therefore, rated as very reliable. Compared to GERG-2008,⁴ the overall AARD is reduced from 0.062% to 0.018%. Another accurate dataset was provided by Ben Souissi et al.¹⁰¹ Although the data were measured with a twosinker magnetic suspension densimeter, which belongs to the most accurate measurement apparatuses, they cannot be represented within their experimental uncertainty of ~0.06% by any of the models. Because the authors measured a mixture with a lower hydrogen concentration than Jaeschke and Humphreys,³⁷ it was tried to fit them within their experimental uncertainty to extend the fitted composition range. However, this attempt caused a loss of accuracy in the description of the Jaeschke and Humphreys³⁷ data, which is why they were finally only fitted with low weights. To investigate this discrepancy, an experimental dataset is being measured at the Ruhr University Bochum, which overlaps both Jaeschke and Humphreys³⁷ data and Ben Souissi et al.¹⁰¹ data in temperature, pressure, and composition. However, the measurements are not completed at this stage and, therefore, the data are not yet available.

Outside the temperature and pressure range of the data by Jaeschke and Humphreys,³⁷ no data with comparable accuracy are available. Up

TABLE 10. AADs (in mol %) of VLE data calculated with the new model and with GERG-2008⁺ for the binary system $CO_2 + H_2$. Nindicates the number of available state points of each publication including pure-fluid data. Both AADs and number of data points are listed for bubble-point data (subscript "x") and dew-point data (subscript "y"). The number of calculated points refers to the new EOS. Pure-fluid data as well as data where deviations in terms of mole fraction could not be calculated were not considered for the AADs

	Ava	ilable	data	Calcu	ılated			This	work	GERG	G-2008
Author	Ν	N_x	N_y	$\overline{N_{x,calc}}$	$N_{y,calc}$	$T_{\min} - T_{\max}$ (K)	$p_{\min}-p_{\max}$ (MPa)	AAD _x	AAD_y	$\overline{AAD_x}$	AAD_y
Augood (1957) ¹⁹	3	3	3	3	3	239.73	18.6-19.3	0.35	3.2	1.1	2.9
Bezanehtak et al. (2002) ⁹²	42	42	34	42	34	278-299	4.8-19.3	1.1	3.0	0.24	6.4
Fandiño <i>et al.</i> (2015) ⁹³	95	95	95	86	86	218-304	0.6-15.4	0.15	0.55	0.58	2.6
Freitag and Robinson (1986) ⁹⁴	7	6	7	6	7	258-274	6.9-27.6	0.39	1.2	1.2	3.2
Jett et al. (1994) ³⁹	9	9	0	9	0	142-189	2.2-5.5	4.3		4.5	
Kaminishi and Toriumi (1966) ⁹⁵	23	21	22	20	21	233-299	5.1-20.0	0.25	1.7	0.83	3.8
Spano <i>et al.</i> (1968) ⁹⁶	58	46	50	46	50	219-290	1.1-20.3	0.22	1.3	0.63	1.2
Tenorio <i>et al.</i> (2015) ⁹⁷	73	37	36	37	36	252-303	2.0-10.5	0.31	0.29	0.85	0.47
Tsankova <i>et al.</i> (2019) ⁹⁸	27	0	27	0	27	249-297	1.9-7.1		0.52		0.35
Tsang and Street (1981) ⁸²	143	138	141	134	138	220-290	0.9-172	0.52	0.78	12	6.3
Tsiklis (1946) ⁹⁹	7	7	7	7	7	273.15	3.9-6.9	2.9	11	2.4	9.4
Yorizane (1971) ⁵⁶	12	11	11	11	11	273.15	6.1-37.5	3.1	2.1	7.5	8.0
Yorizane <i>et al.</i> (1970) ¹⁰⁰	12	11	11	11	11	273.15	6.1-37.5	3.1	2.1	7.5	8.0

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TABLE 11. AARDs and AADs of homogeneous data calculated with the new model and GERG-2008⁴ for the binary system CO₂ + H₂. The corresponding unit of each AAD is given after the respective property. *N* indicates the number of available state points of each publication including pure-fluid data. Pure-fluid data are not considered in the calculation of the overall AARD/AAD

Author	Ν	$T_{\min} - T_{\max}$ (K)	p_{\min} - p_{\max} (MPa)	$x_{\rm CO_2,min} - x_{\rm CO_2,max}$	$AARD_{This \ work}$	AARD _{GERG-2008}				
	Density $p\rho T \bar{x}$									
Ababio and McElroy (1993) ¹⁰⁴	53	303-344	0.13	0.21						
Ben Souissi <i>et al.</i> $(2017)^{101}$	47	273-324	0.5-6.0	0.9464	0.18	0.091				
Bezanehtak et al. (2002) ⁹²	42	278-299	4.8-19.3	0.84-0.99	37	37				
Cheng <i>et al.</i> $(2019)^{103}$	16	673.10	0.6-25.1	0.30-0.40	0.48	0.50				
Cipollina <i>et al.</i> $(2007)^{83}$	48	308-343	20.1-48.9	0.76-0.95	0.53	2.8				
Kritschewsky and Markov (1940) ⁷⁰	54	273-474	5.1-50.7	0.26-0.53	1.4	1.8				
Mallu and Viswanath (1990) ¹⁰²	130	323-424	0.1-6.0	0.14 - 0.77	0.45	0.53				
Pinho <i>et al.</i> $(2015)^{105}$	3	306-307	12.0-12.8	0.80-0.90	6.7	6.9				
Jaeschke and Humphreys (1990) ³⁷	263	274-350	0.2-12.6	0.25-0.50	0.018	0.062				
Sanchez-Vicente et al. (2013) ¹⁰⁶	488	288-334	1.5-22.7	0.90-0.98	1.3	1.4				
Zhang et al. (2002) ¹⁰⁷	20	308.15	5.5-12.9	0.997	2.1	2.4				
2		S	peed of sound w							
Maurer (2021) ⁴⁸	48	249-351	0.5–9.9	0.46-0.75	0.060	0.078				
	Ν	$T_{\min} - T_{\max}$	$x_{\rm CO_2,r}$ (K)	$x_{\rm CO_2,max}$	AAD _{This work}	AAD _{GERG-2008}				
		Second viria	l coefficient B^{a} (cm ³	mol^{-1})						
Brewer (1967) ⁴⁹	3	223-2	.74		5.9	2.5				
Brewer (1967) ⁴⁹	3	223-2	.74		3 ^b	5.1 ^b				
Cottrell <i>et al.</i> (1956) ¹⁰⁹	6	303-3	64	0.5	2.7 ^c	1.3 ^c				
Edwards and Roseveare (1942) ⁸⁰	1	298.1	4		31	31				
Mallu and Viswanath (1990) ¹⁰²	9	323-4	.24 0.	14-0.77	6.4 ^c	7.8 ^c				

^aIf no composition range is given, the dataset contains only the composition-independent B₁₂ and no composition-dependent B.

^bThe composition-independent B_{12} was corrected according to the method given by Garberoglio *et al.*⁵⁰ and the current reference pure-fluid equations.^{15,108}

^cDataset also contains the composition-independent B_{12} .

to 50 MPa, only Cipollina *et al.*⁸³ and Kritschewsky and Markov⁷⁰ provided data. However, both datasets exhibit large scatter and were, consequently, not used for adjusting the parameters of the new model. The high-temperature region up to 474 K was investigated by Mallu and Viswanath¹⁰² and Kritschewsky and Markov.⁷⁰ Since the data of



FIG. 16. p, x-diagram showing VLE data at 235 K, 260 K, and 295.7 K for the binary system CO_2 + H_2 .

Kritschewsky and Markov⁷⁰ scatter with deviations of up to 4% and the data of Mallu and Viswanath¹⁰² show an offset to the data of Jaeschke and Humphreys,³⁷ none of them were used for adjusting the high-temperature region. Within the temperature region of the extended range of validity, Cheng *et al.*¹⁰³ provided 16 density data points at 673 K. However, since the data were only available after completing the equation, they were solely used for validation. For the measurements with a modified Burnett method, the authors specify an expanded uncertainty (*k* = 2) of 0.2 K for temperature, 1.5% for pressure, and 0.8% for density. Except for two data points at pressures above 20 MPa, both the new EOS and the GERG-2008 model⁴ reproduce the data within their combined expanded uncertainty. Overall, almost all available datasets are represented with a lower AARD by the new EOS than by GERG-2008 (cf. Table 11).

In addition to the VLE and homogeneous density data, one speed of sound and four virial coefficient datasets are available. These data were not used for fitting the EOS but only for validation. As with the binary hydrogen mixtures discussed in Secs. 3.1-3.3, the new EOS and the GERG-2008 model⁴ perform similarly and reproduce the data with similar deviations.

4. Physical Behavior

As explained in Sec. 2 and shown in Sec. 3, experimental data are the basis for the development of each equation of state. By adjusting the parameters of the equation to the experimental data, the course of



FIG. 17. Deviation of bubble-point data (top) and dew-point data (bottom) from values calculated with new EOS (left) and GERG-2008⁴ (right) for the binary system CO₂ + H₂. The ordinate is linearly scaled between the dashed lines and logarithmically scaled in the gray filled region.

the Helmholtz energy and thus the course of all properties calculated from it are dictated by the selected data. However, even for experimentally well investigated mixtures, the database covers only parts of the temperature-, pressure-, and composition-dependent state regions. To ensure correct physical behavior in regions not covered by experimental data, various thermodynamic properties and derivatives of the Helmholtz energy were evaluated during the development of the models. In addition to technically relevant state regions, the physical behavior of the equations was also investigated at extreme temperature and pressure ranges in this process. Unreasonable behavior, such as bumps in isolines, was corrected by applying mathematical constraints. By defining the slope and curvature of isolines, qualitatively reasonable results were ensured at conditions outside the range of validity. In Fig. 20, the mixing behavior of methane + hydrogen is shown in two example diagrams for different compositions. Even at temperatures and pressures twice as high as the extended range of validity, the isotherms and isochores are smooth and behave reasonably.

Since similar results were achieved for all investigated mixtures, only the behavior of methane + hydrogen is shown as an example.



FIG. 18. Percentage deviation in density in the homogeneous region between the new EOS and GERG-2008⁴ for the binary system CO₂ + H₂. The white dashed lines represent the normal range of validity of both models, and the black dashed lines mark the phase boundary calculated with GERG-2008. The upper temperature and pressure limits of both axes are based on the extended range of validity for both models. The gray filled area is the two-phase region calculated with the new EOS.



FIG. 19. Percentage deviation of homogeneous density data from the new EOS (left) and GERG-2008⁴ (right) for the binary system CO₂ + H₂. The ordinate is linearly scaled between the dashed lines and logarithmically scaled in the gray filled regions.

However, the lower temperature and upper pressure limit should always be considered in dependence of the pure fluids involved as solids can form at very high pressures and below the triple-point temperature and the equations are only valid for the fluid phase.

A key constraint in the development of the equations was the residual isochoric heat capacity as a function of temperature. Correct physical behavior of this property is the positive curvature of the saturated vapor line and the negative slope of the saturated liquid line away from the critical region. The corresponding vapor isochores should exhibit a negative slope with positive curvature to ensure a correct transition to the ideal-gas limit at high temperatures.¹¹⁰ These constraints led to correct physical behavior of several other properties and were, therefore, applied to all developed equations. In Fig. 21, the residual isochoric heat capacity as a function of temperature is illustrated for the binary system methane + hydrogen at the equimolar composition. All developed departure functions show similar behavior and fulfill the discussed criteria.

Deiters and Bell¹¹¹ showed that a number of the pure-fluid property models employed in the GERG-2008 formulation⁴ result in erroneous critical curves for the mixture. In this case, the erroneous behavior is manifest as a critical curve that has a local

maximum in temperature greater than the temperature of the pure fluid mixed with hydrogen. This erroneous maximum is associated with unphysical phase equilibria. The critical curve tracing routines from Deiters and Bell¹¹² were used to trace the critical curves, starting at the pure fluid. A downside of this approach is that it may miss other critical curves that do not emanate from the pure fluid. The critical curves were traced from the critical pressure of the fluid to 200 MPa. The arclength integration approach was used along with constant-pressure polishing of the solution at each step. The resulting curves are shown in Fig. 22, and the numerical values obtained as well as the standalone code in Python are in the supplementary material. In the cases of methane and CO₂, unphysical maxima are seen at pressures slightly above those of the pure components. Deiters and Bell¹¹¹ showed that this physical defect of the mixture model is probably a consequence of the purefluid equations of state, not the mixture model itself. The critical data points^{17,18,81,82} in Fig. 22 were not used for adjusting the parameters of the new models because they were obtained by extrapolating saturated liquid and vapor data points and were not determined experimentally. However, since the models were fitted to the experimentally determined saturated vapor and liquid data, they also show good agreement with the critical data points.





FIG. 20. ρ , ρ -diagram (top) and ρ , *T*-diagram (bottom) calculated with the new EOS in REFPROP¹² for the binary system CH₄ + H₂ at different compositions. The mixing behavior is shown for pressures up to 200 MPa and temperatures up to 1500 K.

5. Conclusion

Four binary-specific equations of state explicit in the Helmholtz energy were presented for the binary systems of hydrogen with methane, nitrogen, carbon monoxide, and carbon dioxide. The fundamental mathematical structure of the developed mixture models corresponds to the GERG-2008 model⁴ and was extended by modified Gaussian bell-shaped terms.¹⁰ While only the binary mixture methane + hydrogen is described with a departure function in the GERG-2008 model, new departure functions were developed for each of the investigated mixtures. Based on a more comprehensive database and new fitting techniques, a significantly better representation of the VLE data was achieved and the impact of the shifted phase boundaries on the homogeneous region was analyzed. The homogeneous region was mainly adjusted to the available density data, but other properties were also used for validation. In addition to accurately representing the experimental data, reasonable physical behavior of the models was ensured by the analysis of numerous thermodynamic properties.



FIG. 21. c'_{v} , *T*-diagram calculated with the new EOS in REFPROP¹² for the binary system CH₄ + H₂ at the equimolar composition and isochores up to 40 mol dm⁻³.



FIG. 22. *p*, *T*-diagram showing the critical curves of the binary mixtures $CH_4 + H_2$, $N_2 + H_2$, $CO + H_2$, and $CO_2 + H_2$ calculated with the new EOS and GERG-2008.⁴

The normal range of validity covers temperatures of 90 K \leq *T* \leq 450 K and pressures of *p* \leq 35 MPa and is, therefore, equal to the normal range of validity of GERG-2008.⁴ The same applies to the extended range of validity, which covers temperatures of 60 K \leq *T* \leq 700 K and pressures of *p* \leq 70 MPa.

For further improvements and a more comprehensive validation, new highly accurate data are required. Especially for the binary system carbon monoxide + hydrogen, accurate data within the homogeneous region would be of great benefit.

Test values calculated with CoolProp¹⁴ of the mixture models for computer implementation are given in Table 12. The number of digits of the properties is not related to the uncertainty of the model.

TABLE 12.	Test values in the single-phase region for the molar composition of hydrogen x	$H_2 = 0.4$ for computer implementation. For the reproduction of these value	s, the pure-fluid
equations g	iven in Table 1 have to be used	-	

<i>T</i> (K)	$\rho \pmod{m^{-3}}$	p (MPa)	$c_p (\mathrm{J} \mathrm{mol}^{-1} \mathrm{K}^{-1})$	$w (m s^{-1})$	$h (J \text{ mol}^{-1})$	$s (J \text{ mol}^{-1} \text{ K}^{-1})$	$a (J \text{ mol}^{-1})$
			me	thane + hydrogen			
150	500	0.600 550 622	31.833 632 3	398.992 879 9	-1633.134 091	11.691 361 17	-4587.939 512
150	30 000	68.347 691 57	40.818 849 53	1321.412632	-4362.150 985	-39.989 633 21	-641.962 388 7
250	20 000	54.335 545 54	43.160 715 94	949.346 793	-284.051 114 1	-16.391 130 26	1096.954174
400	2 000	6.726 785 283	37.470 800 34	662.291 453	6471.618 216	23.256 964 43	-6194.560 198
			niti	rogen + hydrogen			
90	500	0.356514001	28.522 017 62	243.680 170 3	-2776.388493	4.122 689 122	-3860.458515
90	30 000	29.140 789 01	41.261 865 57	844.817 823 9	-5236.548 963	-48.26292398	-1864.245439
250	20 000	65.607 437 18	35.760 728 68	759.517 681 1	1446.925 315	-14.65720406	1830.854 471
400	2 000	6.865 680 124	30.058 585 35	536.102 457 4	6103.777 267	21.798 899 92	-6048.622763
			carbon	monoxide + hydro	ogen		
100	500	0.398 173 739	28.358 268 77	257.179 460 1	-2511.716 106	6.070 771 38	-3915.140721
100	30 000	26.399 990 72	44.103 076 93	743.020 654 5	-5188.540727	-44.96285504	-1572.254913
250	20 000	62.381 266 62	37.099 400 12	727.582 805 2	1188.425 584	-14.71186292	1747.327 983
400	2 000	6.854 666 627	30.186 717 68	535.565 872 9	6089.343 35	21.791 529 97	-6054.601952
			carbon	n dioxide + hydrog	en		
260	500	1.046 937 897	34.889 446 65	322.078 744 3	1650.155 143	23.962 254 65	-6673.906858
260	28 000	85.165 863 37	51.966 498 29	803.753 283 1	-3460.609 571	-26.906 992 51	493.570 503 5
350	20 000	69.133 173 65	52.295 725 09	639.915 528 2	1167.536 878	-9.433 365 339	1012.556 064
400	2 000	6.489 091 224	39.904 816 56	400.626 192 1	6191.312 059	23.188 126 45	-6328.484 133

Using REFPROP¹² for validation leads to slightly different values (differences of about 1 ppm) since REFPROP Version 10¹² uses the current reference gas constant¹¹³ for most pure-fluid calculations, whereas CoolProp¹⁴ uses the gas constant specified in the corresponding publication of the pure-fluid equation. For mixture calculations, CoolProp¹⁴ calculates the gas constant as the mole-fraction-averaged values of the pure components.

6. Supplementary Material

See the supplementary material for mixture model parameters for the current reference pure-fluid equations and the critical-curve tracing routine as a standalone code in Python.

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Data Availability

Data sharing is not applicable to this article as no new data were created in this study.

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