

SHORT COMMUNICATION

## Equation of State of a Fluid H<sub>2</sub>O-CO<sub>2</sub> at Temperatures 50–350 °C and Pressures 0.2–3.5 kbar

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### ABSTRACT

An equation of state (EOS) was obtained that accurately describes the thermodynamics of the system H<sub>2</sub>O–CO<sub>2</sub> at temperatures of 50–350 °C and pressures of 0.2–3.5 kbar. The equation is based on experimental data on the compositions of the coexisting liquid and gas phases and the Van Laar model, within which the values of the Van Laar parameters  $A_{12}$  and  $A_{21}$  were found for each experimental  $P$ - $T$  point. For the resulting sets  $A_{12}(P,T)$ ,  $A_{21}(P,T)$ , approximation formulas describing the dependences of these quantities on temperature and pressure were found and the parameters contained in the formulas were fitted. This two-stage approach made it possible to obtain an adequate thermodynamic description of the system, which allows, in addition to determining the phase state of the system (homogeneous or heterogeneous), to calculate the excess free energy of mixing of H<sub>2</sub>O and CO<sub>2</sub>, the activities of H<sub>2</sub>O and CO<sub>2</sub>, and other thermodynamic characteristics of the system. The possibility of such calculations creates the basis for using the obtained EOS in thermodynamic models of more complicated fluid systems in  $P$ - $T$  conditions of the middle and upper crust. These fluids play an important role in many geological processes including the transport of ore matter and forming hydrothermal ore deposits, in particular, the most of the world's gold deposits. The knowledge of thermodynamics of these fluids is important in the technology of drilling oil and gas wells. In particular, this concerns the prevention of precipitation of solid salts in the well.

**Keywords:** High Pressure; Elevated Temperature; Water-Carbon Dioxide Fluid; Equation of State

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## 1. Introduction

In the natural geological processes of the upper crust, aqueous fluids play an extremely important role as carriers of substances dissolved in them. Knowledge of the thermodynamics of these fluids is important for understanding and studying hydrothermal processes, including the deposition of ore matter. In addition to the problems of the formation of upper crust rocks, the thermodynamics of subcritical fluids is of practical importance in the technology of drilling oil and gas wells. Technical applications require fairly high accuracy in determining the parameters of fluids, especially the conditions of phase transitions, such as the separation of a fluid into coexisting phases or the precipitation of solid salt in aqueous-salt fluids.

Carbon dioxide is one of the most common components of geological fluids. In this work, we consider the system  $\text{H}_2\text{O}-\text{CO}_2$  at temperatures below the critical point of water and moderately high pressures above 200 bars. Currently, there is a number of both experimental and theoretical works on the properties of the  $\text{H}_2\text{O}-\text{CO}_2$  system, primarily on its phase state and the compositions of coexisting phases. References to experimental works are given in [1–5]. The most recent references can be found in [6, 7]. Among the theoretical works related to the range of temperatures and pressures we selected, it is appropriate to point out the works [1, 3, 4]. These works are based on relatively complicated thermodynamic models. However, they do not provide an accurate reproduction of the experimental data over the entire  $P$ - $T$  range chosen for this study. The comparison with our results is given in the sections below.

Among the experimental works related to the range of temperatures and pressures we selected, the most informative are works containing data on the composition of both, liquid and gas, coexisting phases. The presence of such information greatly simplifies the construction of the EOS. Detailed experimental studies of such kind were made in works [8–10]. The results on the composition of the aqueous phase obtained in these works are in good agreement with each other. However, the data on the composition of the gas phase presented in [9], and in [8–10] differ markedly. In this work, following the arguments of [3, 4], we relied on experimental results [9].

The aim of this work was to develop an empiric EOS for the  $\text{H}_2\text{O}-\text{CO}_2$  system that describes experimental data on the phase state of the fluid with sufficient accuracy. Our

preference was also the theoretical simplicity of the EOS which should make it easy for including into thermodynamic models of systems water-gas-salt. First of all, they are models for  $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$  and  $\text{H}_2\text{O}-\text{CO}_2-\text{CaCl}_2$  systems, developed on the basis existing models of binary water-salt systems [11, 12]. The availability of experimental data on compositions of two coexisting phases makes it reasonable to apply Van Laar model, which is widely used for such two-phase systems [13]. Despite the use of a simple Van Laar model it was possible to achieve accurate reproduction of the experimental results over a wide range of  $P$ - $T$  conditions due to a multi-parameter approximation of the  $P$ - $T$  dependencies of Van Laar parameters  $A_{12}$  and  $A_{21}$ .

## 2. Methods

The EOS of the  $\text{H}_2\text{O}-\text{CO}_2$  system presented in this work is expressed in terms of the Gibbs free energy. The Gibbs free energy per mole of the fluid  $G$  [J/mol] looks like

$$G = x_1 G_1^0 + x_2 G_2^0 + G^{\text{mix}}, \quad (1)$$

where  $x_1 = x_{\text{H}_2\text{O}}$  and  $x_2 = x_{\text{CO}_2}$  are the mole fractions of  $\text{H}_2\text{O}$  и  $\text{CO}_2$  in the mixture.  $G_1^0$  and  $G_2^0$  are the Gibbs free energies of one mole of water and carbon dioxide at given temperatures  $T$  and pressures  $P$ . The Gibbs free energy of mixing  $G^{\text{mix}}$  consists of entropy and energy terms

$$G^{\text{mix}} = RT(x_1 \ln x_1 + x_2 \ln x_2) + G_{\text{wg}} \quad (2)$$

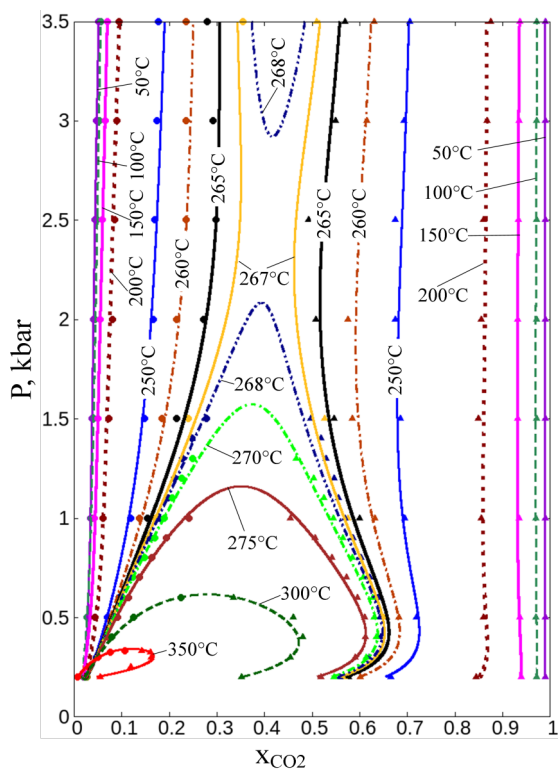
Here  $T$  is in Kelvin,  $R = 8.3144598$  J/mol/K is the universal gas constant. The energy term  $G_{\text{wg}}$  was taken in the form of the Van Laar equation. This equation is widely used to describe the liquid-gas equilibrium for mixtures of substances. For the Gibbs free energy of mixing of two substances, the equation has the form

$$G_{\text{wg}} = RT \frac{A_{12} x_1 A_{21} x_2}{A_{12} x_1 + A_{21} x_2}, \quad (3)$$

where  $A_{12}$  and  $A_{21}$  are parameters determined on the basis of experimental data. The known compositions of the coexisting liquid and gas phases of two substances make it possible to unambiguously determine the parameters  $A_{12}$  and  $A_{21}$ . In the literature, the values of  $A_{12}$  and  $A_{21}$  are determined for a large number of pairs of chemical compounds [13]. A numerical thermodynamic description of supercritical fluids  $\text{H}_2\text{O}-\text{CO}_2$ ,  $\text{H}_2\text{O}-\text{N}_2$ ,  $\text{H}_2\text{O}-\text{H}_2$ ,  $\text{H}_2\text{O}-\text{CH}_4$ ,  $\text{H}_2\text{O}-\text{CO}$ ,

$\text{H}_2\text{O}-\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}-\text{O}_2$ ,  $\text{H}_2\text{O}-\text{Ar}$ , and  $\text{H}_2\text{O}-\text{NH}_3$  using the simplified Van Laar equation was obtained in works<sup>[14, 15]</sup>. For our system, the known compositions of the coexisting liquid and gas phases of two substances make it possible to unambiguously determine the parameters  $A_{12}$  and  $A_{21}$ .

In **Figure 1**, the dots represent the compositions of the coexisting phases experimentally obtained in<sup>[9]</sup>. For each combination of the temperature and pressure, there is a pair of dots corresponding to the compositions of the liquid (left) and gas (right) phases. For each of these pairs, we found the values of parameters  $A_{12}$  and  $A_{21}$  so that the EOS (2)–(3) ensures the decay of the system into two coexisting phases with compositions coinciding with those obtained in the experiment. In **Figure 2**, the dots represent the values of parameters  $A_{12}$  and  $A_{21}$  obtained for experimental points at temperatures of 100 °C, 200 °C and 300 °C and pressures from 0.2 to 3.5 kbar.



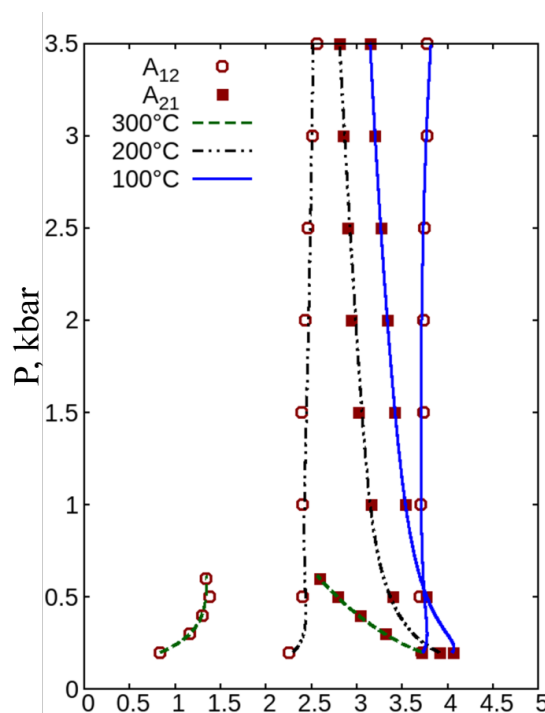
**Figure 1.** Experimental data<sup>[9]</sup> on the compositions of the coexisting liquid ● and gas π phases of  $\text{H}_2\text{O}-\text{CO}_2$  (dots) and the results given by the EOS (1)–(4) (lines).

After an array of  $A_{12}$  and  $A_{21}$  values has been obtained for all experimental points on the compositions of coexisting phases obtained in<sup>[9]</sup>, the task of constructing an EOS is reduced to creating approximating formulas or an algorithm for obtaining  $A_{12}$  and  $A_{21}$  values over the entire temperature

and pressure range studied in the experiment. This mathematical problem is much simpler than constructing the EOS for  $G^{\text{mix}}$  from scratch. For the values of  $A_{12}$  and  $A_{21}$ , the same formulas were used with separate arrays of values of the fitting parameters ( $r_k, s_k, u_k$ ) for  $A_{12}$  and  $A_{21}$ :

$$\begin{aligned}
 A_{ij} = & (r_1 + r_2/V_1 + r_3/V_2 + r_4/(V_1V_2) \\
 & + r_5/V_2^4 + r_6/V_1^4 + r_7/V_1^5V_2 + r_8/(V_1^5V_2^5))/T \\
 & + (s_1 + s_2/V_1 + s_3/V_2 + s_4/(V_1V_2) + s_5/V_2^4 \\
 & + s_6/V_1^4 + s_7/V_1^5V_2 + s_8/(V_1^5V_2^5)) \\
 & + (u_1 + u_2/V_1 + u_3/V_2 + u_4/(V_1V_2) + u_5/V_2^4 \\
 & + u_6/V_1^4 + u_7/V_1^5V_2 + u_8/(V_1^5V_2^5))/T^2
 \end{aligned} \quad (4)$$

where  $V_1$  and  $V_2$  in (4) are the molar volumes of water and  $\text{CO}_2$  at the corresponding temperatures and pressures. These volumes were calculated using the IAPWS95 EOS<sup>[16]</sup> for water and the EOS<sup>[17]</sup> for  $\text{CO}_2$ . The values of the parameters ( $r_k, s_k, u_k$ ) obtained by fitting arrays of  $A_{12}$  and  $A_{21}$  are given in **Table 1**. The results of applying formulas (4) for approximation of  $A_{12}$  and  $A_{21}$  at temperatures of 100 °C, 200 °C and 300 °C are shown by lines in **Figure 2**. It can be seen that Equation (4) provide a smooth and accurate approximation of  $P$ - $T$  dependencies of Van Laar parameters.



**Figure 2.** Parameters  $A_{12}$  and  $A_{21}$ , obtained from experimental results<sup>[9]</sup> (dots), for temperatures of 100 °C, 200 °C and 300 °C and their approximation by the formulas (4) – lines.

The formula (4) include mainly negative powers of  $V_1$ ,  $V_2$ , and  $T$ . This form was chosen to be useable for a reasonable extrapolation. The provided form of Equation (4) was obtained by selecting from some number of test variants. Parameters ( $r_k, s_k, u_k$ ) are coefficients in the approximating equations.

The contents of this section can be summarized as follows:

- The Van Laar model is convenient for constructing EOSs for fluid systems with two coexisting phases.
- Obtaining the parameters  $A_{12}$  and  $A_{21}$  for each  $P$ - $T$  point simplifies the construction of equations for  $G(P,T)$ , reducing the problem to a numerical approximation of  $A_{12}(P,T)$ ,  $A_{21}(P,T)$ . In the temperature and pressure ranges where the fluid is homogeneous, the Van Laar equation may also be valid, but this simple approach of obtaining equations for  $A_{12}(P,T)$  and  $A_{21}(P,T)$  cannot be applied.
- The equation for the full Gibbs free energy of the system  $G(P,T)$  consists of formulas (1)–(4) and: (a) numerical parameters of **Table 1**; (b) Equations of the work<sup>[16]</sup> for  $G_1^0$  and  $V_1$ ; (c) Equations of the work<sup>[17]</sup> for  $G_2^0$  and  $V_2$ .
- Equation for the Gibbs energy of mixing  $G^{\text{mix}}(P,T)$  is given by formulas (2)–(4) in analogous way.

**Table 1.** Values of approximation (4) parameters for quantities  $A_{12}$  and  $A_{21}$ .

	$A_{12}$	$A_{21}$
$r_1$	264756.484135256	223635.416460754
$r_2$	-6612911.77966308	-6144507.89637875
$r_3$	5699049.24588311	17232754.001732
$r_4$	-94399460.1163647	-342036748.098775
$r_5$	-3639508383.07789	56374539230.1375
$r_6$	8120437104.64643	14240821933.6816
$r_7$	37654294.4900813	-36922227.1378313
$r_8$	1.24904046920601E+18	6.27047273773304E+17
$s_1$	-185.291977215905	-145.400397609745
$s_2$	4964.07945837228	4860.08286226492
$s_3$	-6184.89822015764	-20768.8465404253
$s_4$	79073.5506827872	389991.123894993
$s_5$	14999581.7104114	-56449239.0185694
$s_6$	-2674743.35462222	-11898576.6608407
$s_7$	-91193.9602409996	155845.115426557
$s_8$	-1.99414645141056E+15	-1.17360965911632E+15
$u_1$	-93059247.4221783	-79404357.703433
$u_2$	2154884241.00187	1850253757.25515
$u_3$	-784959026.200736	-2737595149.14542
$u_4$	15505319336.2365	58092604195.2549
$u_5$	-2981740833331.74	-14886191888673.1
$u_6$	-2655242520941.67	-3108576495687.0
$u_7$	1816974868.85156	-11837851577.0382
$u_8$	-1.52673758099075E+20	-6.78477967857836E+19

### 3. Results

In the previous section we obtained formulas for calculation the Gibbs free energy of the system  $G(P,T)$ . These equations form the EOS presented in this work. The results of applying our EOS to determine the compositions of coexisting fluid phases are presented by lines in **Figure 1**. This plot shows a good agreement between our EOS and the experimental data. The rather large number of fitting parameters in Equation (4) is a reflection of a complex nature of molecular interactions in a real system. Similarly, the EOSs of pure substances, which provide sufficient accuracy for technical applications, in particular<sup>[16, 17]</sup>, also contain a large number of empirical parameters.

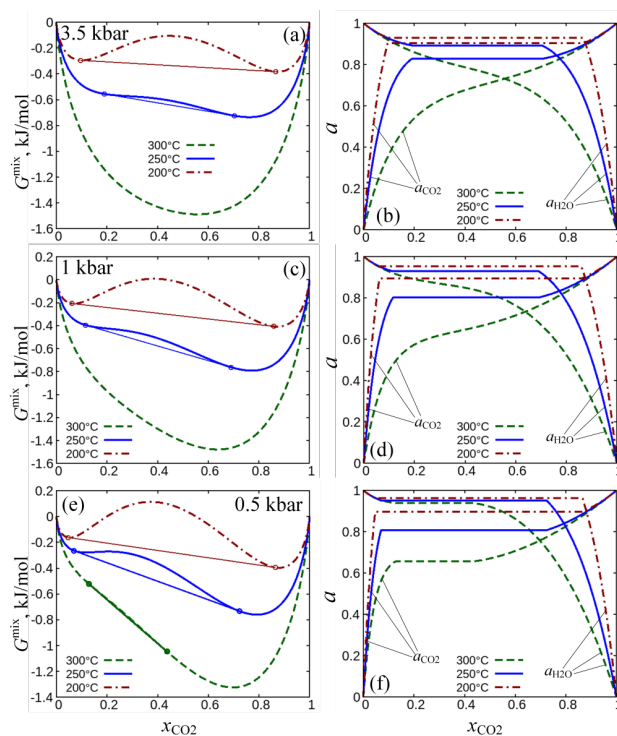
To obtain the parameters of **Table 1**, we used all experimental data<sup>[9]</sup> on the compositions of the coexisting liquid and gas phases. The pressure values corresponding to critical points of the H<sub>2</sub>O–CO<sub>2</sub> fluid, which are also given in<sup>[9]</sup>, were not used. According to the dependences we obtained from the compositions of coexisting phases, the critical points for temperatures of 267–275 °C given in<sup>[9]</sup> lie in the two-phase region. The critical points given by our EOS correspond to higher pressures. This discrepancy can be explained by the difficulty of direct experimental determination of the parameters of critical points. The extremely small difference in the free energies between the homogeneous and two-phase states of the system near the critical point leads to an extremely slow establishment of phase equilibrium, which not always can be achieved under specific experimental conditions. The same experimental difficulties can explain the absence of experimental results for liquid and gas phases that are sufficiently close in composition when approaching the critical points for temperatures of 267–275 °C. Our EOS predicts the occurrence of the second critical point for the system H<sub>2</sub>O–CO<sub>2</sub> at the temperature of 268 °C (**Figure 1**).

As can be seen from **Figure 1**, the experimental results for the entire pressure range from 0.2 kbar to 3.5 kbar are available for temperatures not exceeding 267 °C. Allowing for some extrapolation, we assume the possibility of using our EOS over the entire pressure range for temperatures up to 300 °C. Experimental data for the temperature of 350 °C are available up to a pressure of 0.325 kbar. The critical point given by equation (1)–(4) for this temperature corresponds to a pressure  $P_{350} = 0.341$  kbar. For a temperature of 350 °C, applying equations (1)–(4) above this point is an extrapolation

that appears to be quite reliable up to the critical point for a temperature of 300 °C, i.e.,  $P_{300} = 0.615$  kbar.

Comparison with existing models, for example<sup>[1, 3, 4]</sup>, shows a better agreement with experimental data of our EOS. The model<sup>[1]</sup> relates to the composition the liquid phase only and is limited by  $P \leq 2$  kbar. The relative recent work<sup>[4]</sup> is focused on the same experimental data<sup>[9]</sup>, but the model presented there reproduces experimental data rather poorly for temperatures above 275 °C. The range of pressures in work<sup>[4]</sup> is limited by  $P \leq 2$  kbar. Thus, the entire pressure range containing the second critical point of the system H<sub>2</sub>O–CO<sub>2</sub> and characterized by the growing gap of miscibility between the liquid and gas phases is not covered by the model. The earlier work<sup>[3]</sup> shows a greater discrepancy with experimental data on the composition of coexisting phases within a limited range of pressures  $P \leq 1$  kbar. The discrepancies with the experiment could be explained by the difference in approaches to the development of EOS in works<sup>[3, 4]</sup> and in the current work. The EOSs of<sup>[3, 4]</sup> are based on preliminary chosen thermodynamic models containing limited numbers of fitting parameters. The goal of our approach was to accurately reproduce the experimental data using a very simple thermodynamic model, but with sufficient fitting parameters to describe the  $P$ - $T$  dependences.

The EOS, expressed in terms of the Gibbs free energy of mixing, makes it possible to calculate various thermodynamic quantities that are not presented among the experimental results used to obtain the parameters of **Table 1**. Examples of calculations of the Gibbs free energy of mixing and activities of components depending on the mole fraction of CO<sub>2</sub> in the system H<sub>2</sub>O–CO<sub>2</sub> are given in **Figure 3**. Figures in the left column show the  $G^{\text{mix}}(x_2)$  dependences given by Equations (2)–(4) for temperatures of 200 °C, 250 °C, and 300 °C and pressures of 3.5, 1.0, and 0.5 kbar. In cases where the nature of this dependence leads to the division of the system into two coexisting phases, these graphs also show tie lines connecting the points corresponding to the compositions of these coexisting phases. In the Figures in the right column, for the same temperatures and pressures, the dependences of the activities of the components on the mole fraction of CO<sub>2</sub> in the system are given. In cases where there are two coexisting phases in the system, the values of activities are related to the compositions of these phases.



**Figure 3.** Dependences of the thermodynamic parameters of the H<sub>2</sub>O–CO<sub>2</sub> system on the mole fraction of CO<sub>2</sub> at  $P = 3.5$  kbar (a,b),  $P = 1$  kbar (c,d), and  $P = 0.5$  kbar (e,f). (a,c,e) the Gibbs free energy of mixing according to formulas (2)–(4); straight lines with dots at the ends are tie lines; (b,d,f) activities of H<sub>2</sub>O and CO<sub>2</sub>.

## 4. Conclusions

- For the fluid system H<sub>2</sub>O–CO<sub>2</sub> at pressures of 0.2–3.5 kbar and temperatures below the critical point of water, an EOS was constructed. Our EOS precisely reproduces experimental data on the compositions of the coexisting liquid and gas phases by Tödheide and Franck<sup>[9]</sup>. Our EOS is grounded on the Van Laar model, which allows, on the basis of data on the compositions of two coexisting phases, to unambiguously determine the values of two parameters of the model  $A_{12}$  and  $A_{21}$  for each  $P$ - $T$  point. This made it possible to determine the dependence of the Gibbs free energy of mixing  $G^{\text{mix}}$  on the mole fraction of CO<sub>2</sub> in the system for each experimental combination of temperature and pressure. For the dependences of the values of  $A_{12}$  and  $A_{21}$  on temperature and pressure, approximation formulas are constructed, expressed in terms of temperature and molar volumes of water and carbon dioxide.

- The dependence  $G^{\text{mix}}(P, T, x_{\text{CO}_2})$  was obtained, which makes it possible to determine the phase state of the system (homogeneous or heterogeneous) for arbitrary values of  $P$  and  $T$ , as well as to calculate other thermodynamic characteristics of the system.
- The possibility of such calculations creates the basis for the use of the resulting EOS in thermodynamic models of more complex fluid systems. Such systems, in particular containing salts like NaCl, CaCl<sub>2</sub>, etc., play an important role in the processes of metamorphism and metasomatism, as well as in transfer of ore matter and forming hydrothermal deposits of gold and a number of other metals. Detailed information on the physical and chemical properties of fluids is important both from a general geological point of view and for the exploration and evaluation of ore deposits. The same knowledge of the physical and chemical properties of fluids is also important for technical applications in oil and gas well drilling technology. In particular, to prevent precipitation of solid salts in the well. The latter has both economic and environmental value.
- The possible following development of the EOS presented above consists in an additional fitting on experimental  $PVTx$  data for both increasing the precision of the EOS and expanding the region of its applicability onto temperatures above the critical point of water. This development is important for obtaining more adequate equations for both subcritical and supercritical fluids<sup>[18–20]</sup>. It can also help in better understanding the phase behavior of the of H<sub>2</sub>O–CO<sub>2</sub> system both in the subcritical region (second critical point and growing the two-phase field at high pressure) and its phase behavior in the supercritical region<sup>[21]</sup>.

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## Institutional Review Board Statement

Not applicable.

## Informed Consent Statement

Not applicable.

## Data Availability Statement

The experimental data used in the study are available in the paper Tödheide, K., Franck, E.U., 1963. The two-phase region and the critical curve in the carbon dioxide-water system up to pressure of 3500 bar. *Zeitschrift für Physikalische Chemie Neue Folge.* 37, 387–401. DOI: [https://doi.org/10.1524/zpch.1963.37.5\\_6.387](https://doi.org/10.1524/zpch.1963.37.5_6.387).

A computer program that performs calculations with the presented equation of state is available in the public domain: [https://www.dropbox.com/scl/fi/8iaj03dtg09a0f4wer6ow/H\\_2O\\_CO\\_2\\_VL2024.ZIP?rlkey=b54a6ledmf63cuu6qn1lvtgzuz&st=2eaqj4u&dl=0](https://www.dropbox.com/scl/fi/8iaj03dtg09a0f4wer6ow/H_2O_CO_2_VL2024.ZIP?rlkey=b54a6ledmf63cuu6qn1lvtgzuz&st=2eaqj4u&dl=0).

## Conflict of Interest

The author declares no conflict of interest.

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