

Article

Experimental and Theoretical Study on the Solubility of High-Temperature, High-Pressure, High-CO₂ Natural Gas in Formation Water

Shuheng Cui ¹, Hao Liang ², Zhichen Deng ^{3,*}, Jie Kong ¹, Qilin Wu ³ and Kun Xu ³

¹ Engineering Technology Zhanjiang Branch, CNOOC Energy Development Co., Ltd., Zhanjiang 524057, China; cuihhh@cnooc.com.cn (S.C.)

² Hainan Branch, CNOOC (China) Co., Ltd., Haikou 570100, China

³ College of Petroleum Engineering, Guangdong University of Petrochemical Technology, Maoming 525000, China; wuqilin9@gdupt.edu.cn (Q.W.)

* Correspondence: dengzhichen@gdupt.edu.cn; Tel.: +86-13302512241

Abstract

To support drilling gas influx control, saline aquifer CO₂ sequestration and CCUS development under the dual carbon goals, this study proposes a high-precision calculation method for the solubility of high-temperature, high-pressure, CO₂-rich natural gas in formation water. An activity–fugacity coupling model is established: fugacity coefficients of gas components are solved via the dimensionless Helmholtz free energy equation of state, and liquid-phase activity coefficients are characterized by the Pitzer electrolyte model. Comparative experiments with three natural gas and three formation water samples are carried out at 393.15–453.15 K and 5–100 MPa to analyze the influences of temperature, pressure, salinity and CO₂ content on solubility for model verification. The overall relative error between calculated and experimental data is below 10% (max 4.5%). Solubility rises rapidly with pressure then plateaus, declines with salinity, and grows with CO₂ content; CO₂ solubility far exceeds that of alkanes. This efficient, widely applicable model cuts engineering costs and guides safe oil-gas exploitation and CCUS deployment.

Keywords: solubility; experiment; model calculation

1. Introduction

Hydrocarbon and acid gas components such as those found in natural gas are common solutes in aqueous solutions. They are ubiquitous in formation waters of petroliferous basins, hydrothermal systems, magmatic melts, and various other geological fluids [1–4]. The factors influencing natural gas solubility are complex [5–8]: temperature, pressure, and salinity, as core factors, directly alter the gas dissolution capacity. Gas–water relative permeability characteristics directly affect the dissolution process by influencing the contact efficiency between gas and liquid phases, thereby regulating the actual dissolved amount [9]. Furthermore, interactions between CO₂ and formation water or rock can indirectly affect the natural gas dissolution equilibrium by altering the ionic composition of the formation water, among other effects [10,11]. Simultaneously, natural gas often contains significant amounts of acid gases. If accurate solubility calculations are lacking after natural gas dissolves into formation water, it can lead to an unclear understanding of reservoir fluid mechanisms, difficulties in accurately evaluating reservoir parameters, and challenges in wellbore safety and flow control, potentially causing downhole packer failures, etc. In the



Academic Editor: Fernando Rubiera González

Received: 21 April 2026

Revised: 8 June 2026

Accepted: 16 June 2026

Published: 27 June 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

field of oil and gas energy, correctly understanding the dissolution capacity of natural gas in formation water is of great significance for understanding natural gas accumulation, exploration, development, and storage/transportation. For instance, CCUS represents a major requirement and a key core technology for China to achieve its “dual carbon” goals and is also a global research hotspot [12].

Regarding research on natural gas solubility in formation water, models primarily include [13] the γ - ϕ model (activity–fugacity model), which employs a hybrid approach where liquid phase behavior is described using an activity coefficient equation, while the fugacity coefficients of gas phase components are calculated by an equation of state. In contrast, the ϕ - ϕ model (fugacity–fugacity model) provides a unified descriptive framework by using a single equation of state to calculate fugacities for both gas and liquid phases to perform phase equilibrium calculations. Additionally, some researchers have proposed molecular simulation methods starting from molecular fundamentals:

- (1) The equation of state method is a primary approach for studying the thermodynamic properties of geological fluids. Currently, commonly used equations of state fall into the following four types: cubic equations of state [14–17], virial-type equations of state [18–20], Statistical Associating Fluid Theory (SAFT) equations of state [21,22], and dimensionless Helmholtz free energy equations of state [23]. Since Van der Waals proposed the Van der Waals equation, many scholars have proposed numerous improved cubic equations of state, using two or more parameters to enhance accuracy in volumetric and phase equilibrium properties [24,25]. In the evolution of cubic equations of state, the Redlich–Kwong (RK) equation represents a significant development [25,26]. Its core improvement lies in applying a temperature correction to the attractive term in the Van der Waals equation, significantly improving its predictive accuracy and making it the first cubic equation of state with important engineering application value. Soave [27] proposed the Soave–Redlich–Kwong (SRK) equation, improving upon the RK equation by modifying the form of parameter “a” to be a function of temperature, greatly enhancing the calculation accuracy and application range of cubic equations. The Peng and Robinson (PR) equation [28,29] further improved accuracy by adding an attractive term based on the SRK equation, enabling it to predict vapor pressure and volumetric properties of pure substances, as well as calculate phase equilibrium and volumetric properties for mixed systems. Cubic equations of state are simple in form and are often used to calculate vapor–liquid equilibrium properties of nonpolar and weakly polar fluids. Virial-type equations of state are expressed as a series expansion of the compressibility factor. Their characteristics include: rigorous derivation from statistical mechanics; relatively many parameters and complex form; high accuracy. Starting from Ursell, researchers gained a microscopic, statistical mechanics perspective on intermolecular forces [30], providing a theoretical basis for subsequently expressing macroscopic pressure–volume–temperature (PVT) relationships of fluids in series form. The Martin–Hou (MH) equation proposed by Martin and Hou [31,32] through analysis of PVT data for different compounds is a representative virial-type equation of state. Kedge and Trebble [33] proposed a virial-type equation of state for calculating thermodynamic properties of pure substances by adding a near-critical region correlation term to the equation. This addition improved the accuracy of calculating PVT properties, saturated liquid density, and vapor–liquid densities for pure fluids. The predictive accuracy of the equation of state method is influenced not only by the chosen equation but also by the mixing rules employed. When fewer parameters are introduced and universal or simple mixing rules are used, the form is simple and calculation is convenient, but accuracy is lower; when more parameters are introduced and complex mixing rules are used,

accuracy improves correspondingly, but this affects the equation's simplicity and ease of use. The SAFT equation of state [34] is widely used for calculating thermodynamic properties of fluid mixtures due to its solid statistical mechanics foundation, enabling calculation of thermodynamic properties for some complex fluids, including chains, aromatics, chlorinated hydrocarbons, esters, alkanols, and carboxylic acids. To further improve predictive accuracy, Gross et al. [35] refined the SAFT equation of state using perturbation theory, proposing the Perturbed-Chain + Statistical Associating Fluid Theory (PC-SAFT) equation of state. These molecular-based equations of state, having clear physical significance, offer more reliable extrapolation capabilities and more accurate predictions compared to traditional empirical models. The dimensionless Helmholtz free energy equation of state is expressed as a power series in reduced temperature and reduced density, primarily consisting of an ideal part and a residual part. This type of equation of state was developed based on equations established by Schmidt and Wagner, Jacobsen et al. [36]. Helmholtz free energy equations of state are renowned for their high accuracy and wide effective temperature range, capable of comprehensively deriving all thermodynamic properties of a fluid. Particularly important is that they avoid cumbersome integration operations during derivation, making the entire calculation process more efficient, thereby significantly reducing computational load. They are commonly used to calculate thermodynamic properties of hydrocarbon mixed gases.

- (2) The activity coefficient method is theoretically based on solving for fugacity coefficients of gas phase components using an equation of state [37,38], while characterizing the non-ideality of the liquid phase with an activity coefficient equation, thereby constructing a complete phase equilibrium calculation framework. Traditional models, such as Wohl-type equations [39,40], local composition models, and group contribution models, perform well at atmospheric pressure. However, due to their insufficient description of pressure effects, their applicability significantly decreases under high system pressures.
- (3) Molecular simulation methods: Statistical Associating Fluid Theory is based on Wertheim's first-order perturbation theory [41,42]. The reason such equations of state exhibit excellent predictive and extrapolative capabilities lies in the physical clarity of their parameters. This allows them to deduce macroscopic properties from the basic principles of molecular interactions, surpassing the accuracy and reliability of data-fitting empirical models [43]. Moreover, they can simultaneously calculate phase equilibrium properties and density of systems. Therefore, Statistical Associating Fluid Theory has been successfully applied to thermodynamic property and phase equilibrium calculations for various mixed systems [44,45].

In the field of model construction for predicting the solubility of natural gas and mixed gases, multiple researchers have conducted systematic studies using the PR equation of state combined with different thermodynamic methods. Zirrahi et al. [46] and Ziabakhsh-Ganji and Kooi [47] successively proposed solubility prediction methods for acid gas–brine systems. Both used the PR equation of state to characterize the gas phase and employed the Pitzer activity coefficient model to handle liquid phase non-ideality, constructing thermodynamic models applicable to CO₂–CH₄–H₂S–brine and CO₂–CH₄–N₂–H₂S–SO₂–brine systems, respectively. Venkatraman et al. [48] further extended this approach, maintaining the PR equation for the gas phase while selecting the NRTL activity coefficient model to characterize liquid phase behavior, establishing a calculation framework for the solubility of CO₂–H₂S mixed gases in pure water. It is important to note that the applicable conditions for these models are relatively consistent, with temperature and pressure ranges limited to within 400 K and 80 Mpa, respectively. Simultaneously, Li et al. [49,50] also developed

a prediction tool specifically for CO₂-CH₄-H₂S mixed gases in NaCl aqueous solutions. This scheme modifies intermolecular forces by assigning different interaction parameters to the gas and liquid phases and quantifies the salt effect using an empirical correlation. However, this model shows certain limitations under actual operating conditions with pressures below 60 Mpa and temperatures below 383.15 K. Subsequent scholars have established models capable of calculating the solubility of CO₂-CH₄-N₂ mixed gases. Hajiw et al. [51] simulated the solubility of CO₂ and impurity gases (N₂, CH₄, O₂, NO, etc.) in pure water. This model adopts a γ - ϕ (activity–fugacity coefficient) form, and gas–liquid phase equilibrium calculations use the geochemical model of Corvisier et al. [52]. Hasanpouryouzband et al. [53] experimentally measured and computationally simulated the solubility of CO₂-N₂ mixed gases in pure water and brine, using the CPA-SRK 72 equation, VPT equation, and PC-SAFT equations of state combined with corrected binary interaction parameters to calculate component fugacities.

Based on the theoretical foundation of thermodynamic equations of state, and considering the influence of formation water salinity on system phase equilibrium, this study establishes a gas solubility model through an activity–fugacity coupling approach to improve calculation accuracy. Solubility is then calculated according to gas–liquid phase equilibrium theory.

2. Experimental Apparatus and Methods

2.1. Experimental Samples and Equipment

The gas samples used in the experiments were obtained from field sampling. Due to limited quantities from field samples, the composition of the retrieved gas samples was analyzed, and sufficient experimental samples were prepared in the laboratory according to the component content, as shown in Table 1. The water samples used in the experiments were obtained from field sampling, and filtered to remove impurities, ensuring no crystal precipitation throughout the process. The ion analysis results of the water samples are shown in Table 2. A total of 10 ultra-high-temperature and high-pressure exploration wells were drilled in the study area. Six formations were tested, and data on productivity, pressure, and fluid properties were obtained. The relevant data from formation testing are shown in Table 3.

Table 1. Composition of dissolved natural gas samples.

Sample	N ₂ (%)	CO ₂ (%)	CH ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₈ (%)	iC ₄ H ₁₀ (%)	nC ₄ H ₁₀ (%)	iC ₅ H ₁₂ (%)	nC ₅ H ₁₂ (%)	C ₆ H ₁₄ (%)
1	2.38	69.37	28.25	—	—	—	—	—	—	—
2	3.00	11.39	76.04	7.11	1.30	0.39	0.32	0.26	0.13	0.06
3	2.34	15.66	77.05	4.95	—	—	—	—	—	—

Table 2. Composition of ion components in dissolved formation water samples.

Sample	Na ⁺ (mg/L)	K ⁺ (mg/L)	Mg ²⁺ (mg/L)	Ca ²⁺ (mg/L)	F [−] (mg/L)	Cl [−] (mg/L)	NO ₃ [−] (mg/L)	SO ₄ ^{2−} (mg/L)	Total Salinity (mg/L)
a	7348.6	736.4	—	100.5	138.8	7113.0	—	2061.7	17,499.0
b	3266.5	650.4	—	60.0	—	3460.9	—	297.5	7735.3
c	3887.1	803.6	—	30.1	—	3609.5	—	326.2	8656.5

Table 3. Relevant data from formation testing.

Well	Test Interval (m)	Choke Size (mm)	Gas Flow Rate (10 ⁴ m ³ /d)	Water Flow Rate (m ³ /d)	Flowing Pressure Drawdown (MPa)	Pressure Drop (%)	Skin Factor	Skin Oil Production Coefficient (MPa)	CO ₂ Content (%)	H ₂ S Content (ppm)	Formation Pressure (MPa)	Pressure Coefficient	Formation Temperature (°C)	Effective Permeability (mD)	Water Productivity Index (m ³ /(d·MPa))
L1	4052.8~4070.0	7.14	12.25	14.5	62.892	70	32	50.49	23.58	0	90.225	2.28	194.1	1.4	0.23
L2	4210.0~4228.9	7.94	2.36	285.9	30.813	33.5	17.6	23.556	68.01	69	92.678	2.235	212.1	0.67	9.28
L3	4235.0~4290.0	11.11	7.3	244.8	62.691	68.8	9.7	33.589	16.39	22	91.381	2.282	207.3	0.523	3.9
L4	4095.0~4115.0	7.14	35.5	40.6	12.239	14.1	8.2	4.45	72.01	47	87.91	2.228	195.3	7	3.32
L5	4051.4~4061.5	3.18	0.79	11.6	62.779	69	16.44	46.841	66.80	24	91.472	2.275	189.4	0.044	0.18
L6	4101.0~4170.5	7.94	0.78	213.1	51.081	54.4	80	46.841	44.40	77	93.985	2.234	215.2	0.064	4.17

Based on the distribution pattern of gas components in the high-temperature and high-pressure natural gas wells in the study area, CO_2 content ranges from 5% to 75%, and CH_4 content ranges from 25% to 89%. Moreover, more than 60% of the wells in the high-temperature and high-pressure block have a CO_2 content of approximately 70%. Therefore, this study fully considers the simulation intervals for different CO_2 and CH_4 contents. According to the actual field conditions, experimental samples were collected on-site at the high-pressure wellhead. After sampling, the contents of various gas components were analyzed, and typical samples were further examined. For some wells, the contents of $\text{C}_2\text{--C}_{6+}$ components were below the detection limit. Due to the limited amount of samples retrieved from the field, subsequent experiments were conducted by preparing sufficient experimental samples based on the component contents measured.

This experiment is an ultra-high-temperature and ultra-high-pressure experiment. The experimental setup is shown in Figure 1. The apparatus mainly consists of a gas chromatograph, a multifunctional ion chromatograph (aqueous phase ion analyzer), an ultra-high-temperature and high-pressure reaction vessel, an ultra-high-pressure displacement pump, a gas–liquid separation device, and a gas flow meter. The system has a maximum pressure rating of 200 MPa and a maximum temperature rating of 473.15 K, meeting the requirements of this study.

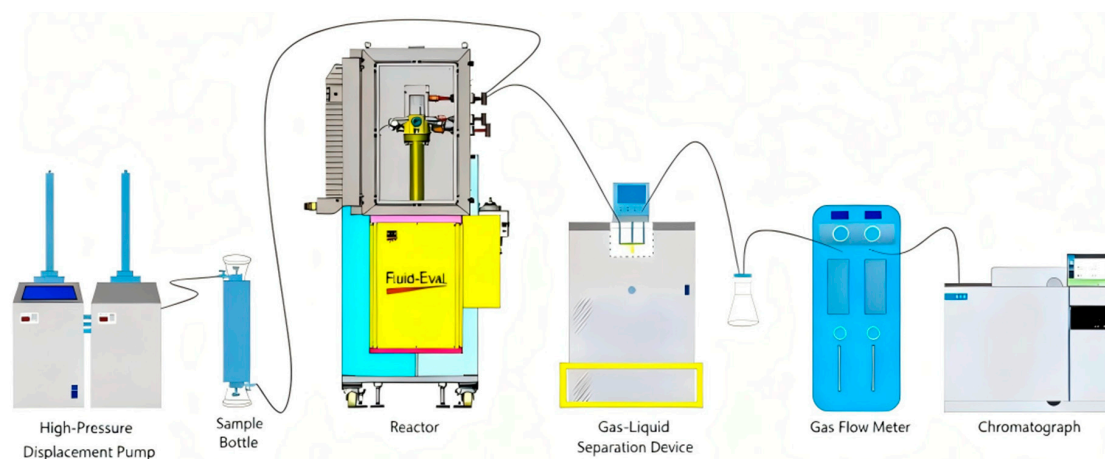


Figure 1. Schematic diagram of natural gas solubility testing process.

The specific instrument parameters are as follows:

- (1) Gas chromatograph: Used to determine the composition of natural gas obtained from the field. Overall performance: retention time reproducibility < 0.01%, peak area reproducibility < 1% RSD; the valve system has independent temperature control, allowing separate control from the column oven to better manage sample state; temperature range: 283.15 K to 693.15 K above room temperature; temperature setting resolution: 273.15 K; flow control: electronic pneumatic control with modes such as constant flow, constant pressure, programmed flow ramp, and programmed pressure ramp; EPC flow accuracy: 0.001 psi.
- (2) Multifunctional ion chromatograph (aqueous phase ion analyzer): Mainly used to determine the salinity and ion content of water samples obtained from the field. Model: ICS-5000 (Thermo Fisher Scientific Inc., Massachusetts, USA). Main functions: The ICS-5000 ion chromatograph uses a conductivity detector for detection, producing chromatograms from which ion contents are calculated. A single injection allows analysis of common anions (F^- , Cl^- , Br^- , NO_3^- , NO_2^- , SO_4^{2-} , PO_4^{3-}), bromate, and cations (Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+). Key specifications: dual-system capillary ion chromatograph with independent temperature control; pump: high-performance,

low-pulsation dual-piston pump with chemically inert, non-metallic, damper-free pump head and PEEK tubing, compatible with eluents of pH 0–14 and reversed-phase organic solvents; flow rate range: ≥ 2.500 mL/min; maximum pressure: 35,500 psi; maximum flow rate error $< 0.1\%$; flow precision: $< 0.1\%$; pressure pulsation: $< 0.2\%$ of system pressure; conductivity detector: temperature compensation function, cell volume < 0.03 μ L; high-capacity high-efficiency separation column (250×0.4 mm) and corresponding guard column (50×0.4 mm); single injection capable.

- (3) Ultra-high-temperature and high-pressure reaction vessel: A multifunctional instrument that, through different configurations, can realize the analysis of dissolved gas/water ratio under ultra-high-temperature and pressure. Reaction vessel: volume 500 mL, pressure rating 150 MPa, temperature rating 473.15 K, temperature control accuracy ± 27.315 K, pressure control accuracy ± 10 psi.
- (4) Ultra-high-pressure displacement pump: Key specifications: constant pressure mode with automatic pump advance and retract; maintains constant pressure within ± 1 psi; digital control panel allows setting of different pressures and speeds for fully automatic operation; special piston capable of withstanding 20,000 psi.
- (5) Gas–liquid separation device: Primarily used for effective separation of gas and water in experiments, employing a condensation method to achieve separation of gas and liquid phases at 243.15 K.
- (6) Gas flow meter: Measures the volume of discharged gas with a measurement accuracy of 1 mL.
- (7) Precision electronic balance: Measures the weight of discharged formation water with an instrument accuracy of 0.0001 g.

2.2. Experimental Conditions and Methods

The experimental conditions primarily included temperature, pressure, different gas component compositions, and water salinity. The experimental temperature range was 393.15–453.15 K, and the pressure range was 5–100 MPa. The gas component compositions and dissolved water salinity are shown in Tables 2 and 3.

The experimental method mainly adopted the single degassing experiment method from the “Analysis of Oil and Gas Reservoir Fluid Properties” (GB/T 26981-2020) [54]. The standard conditions for experimental data detection were set at 293.15 K and 0.101325 MPa according to national regulations. The experimental steps were as follows:

- (1) Sample preparation: pretreatment of water samples involved oil–water separation before the experiment, followed by filtration of impurities from the formation water samples using a specific filter paper for backup. The density of the filtered formation water samples was measured using a densitometer. Gas sample preparation involved determining the component composition of the field-acquired gas samples using a gas chromatograph and replicating this composition indoors. The gas samples were pressurized to the preparation pressure using an ultra-high-pressure intensifier pump.
- (2) Evacuation and sample transfer: the experimental flow path was connected and evacuated. Experimental formation water was transferred into the ultra-high-temperature, high-pressure reaction vessel using a high-precision pump, and the pressure was increased to the preparation pressure. An excess amount of gas sample was injected into the ultra-high-temperature, high-pressure reaction vessel using a high-pressure pump. The pump was slowly retracted to allow the gas sample to enter the vessel gradually. Injection stopped once the preset volume was reached.
- (3) Mixing and equilibration: the experimental temperature was raised to the set temperature, and the system pressure was increased to 100 MPa using an ultra-high-pressure displacement pump, maintaining stable pressure at 100 MPa. The ultra-

high-temperature, high-pressure reaction vessel was then stirred to ensure thorough contact between the formation water and gas. After the entire system stabilized, stirring stopped, and the system was allowed to stabilize for 3–4 h before measuring the dissolved gas–water ratio under those temperature and pressure conditions.

- (4) Dissolved gas–water ratio testing: before measurement, the mass of the separation tube (m_1) was measured using a high-precision balance. The atmospheric pressure (P_1) at that time was recorded. The indoor temperature (T_1) during the experiment was recorded. The gas–liquid separation tube was placed in ice water. While maintaining the experimental pressure, the valve was slowly opened to perform a flash evaporation experiment. The reading on the gas flow meter (V_1) was recorded, and the mass of the liquid meter after the experiment (m_2) was recorded. Three repeated experimental measurements were performed, with the pressure system stabilized for 30 min under conditions fluctuating within ± 1 psi between each measurement. If poor repeatability was observed during the experiment, re-stirring and re-measurement were required until the dissolved gas–water ratio stabilized.
- (5) Testing dissolved gas–water ratio at other experimental pressures: this experiment adopted a method of reducing system pressure to measure the dissolved gas–water ratio at different pressures. After completing the 100 MPa gas–water ratio test, the experimental pressure was set to 90 MPa. After the entire system stabilized, stirring stopped, and the system was allowed to stabilize for 3–4 h before testing the gas–water ratio at that temperature and pressure. This step was repeated to test the gas–water ratio at other experimental pressure points. If, during the experiment at low pressures, retracting the pump could not reduce the pressure to the predetermined level, the gas sample in the high-temperature, high-pressure reaction vessel was vented by orienting the vessel upward until the specified pressure was reached.

2.3. Experimental Design

This study designed a multi-factor comparative experiment, utilizing three types of natural gas samples with different compositions and three types of formation water samples with different salinities. Within the temperature range of 393.15–453.15 K and pressure range of 5–100 MPa, a systematic solubility test was conducted. By measuring the volume of degassed gas and the volume of water after degassing from samples of water saturated with natural gas, core solubility data under different conditions were obtained, as shown in Table 4. To better characterize the variation patterns of carbon dioxide solubility across different temperature–pressure systems, and given that the high CO_2 content is a distinguishing feature of the high-temperature and high-pressure block in this study—while the formation water characteristics of the strata containing high-temperature, high-pressure, CO_2 -rich natural gas closely resemble those of the selected samples—the above-mentioned samples were chosen for representative simulation and evaluation experiments.

Table 4. Experimental testing plan for solubility of natural gas in formation water.

Gas Sample	Water Sample	Test Temperature (K)	Test Pressure (MPa)	Number of Test Points
1	c	393.15, 423.15, 453.15	5, 10, 20, 30, 40, 50, 60, 70, 80, 100	33
2	a	393.15, 423.15, 453.15	5, 10, 20, 30, 40, 50, 60, 70, 80, 100	33
3	B	393.15, 423.15, 453.15	5, 10, 20, 30, 40, 50, 60, 70, 80, 100	33

2.4. Data Processing

Corrected gas volume:

$$V_2 = \frac{P_0 T_1}{P_1 T_1 T_2} \quad (1)$$

where V_2 is the corrected gas volume (mL); V_1 is the volume measured by the gas flow meter (mL); P_1 is the room pressure (MPa); P_0 is the standard atmospheric pressure (MPa); T_1 is the room temperature (K); T_2 is the temperature under standard conditions (K).

Calculate the volume occupied by the water sample:

$$V_3 = \frac{m_2 - m_1}{\rho_1} \quad (2)$$

where m_1 is the mass of the liquid meter before the experiment (g); m_2 is the mass of the liquid meter after the experiment (g); ρ_1 is the density of the water sample (g/cm^3); V_3 is the volume occupied by the water sample (mL).

Calculate the dissolved gas–water ratio:

$$\text{GWR} = \frac{V_2 - V_3}{V_3} \quad (3)$$

where GWR is the dissolved gas–water ratio (cm^3/cm^3).

Determine the value of the dissolved gas–water ratio:

The dissolved gas–water ratio is taken as the average of three measurements. If one measurement differs significantly from the other two, an additional experiment is conducted, and the average of the three closest data sets is taken.

3. Experimental Results and Analysis

3.1. Influence of Temperature and Pressure on Natural Gas Solubility

As shown in Figure 2, test results for Gas Sample 1 and Water Sample c (salinity 8656.5 mg/L) indicate that, under constant temperature conditions, the relationship between natural gas solubility and pressure is overall nonlinear. However, it exhibits piecewise linear characteristics within two intervals: 5–20 MPa and 40–100 MPa. Specifically, in the low-pressure stage of 0–20 MPa, solubility increases rapidly with rising pressure. When pressure exceeds 40 MPa and enters the high-pressure stage, the growth momentum weakens significantly, and the increase tends to level off. Comparison of the curve slopes clearly reveals the distinctly different growth rates in these two stages. Furthermore, solubility shows a positive correlation with temperature: the higher the temperature, the greater the solubility, and the corresponding equilibrium pressure required to achieve the same dissolution level also increases. This temperature–pressure coupling effect is the fundamental reason for the significant differences in solubility that may occur between different well sections within the same oilfield block.

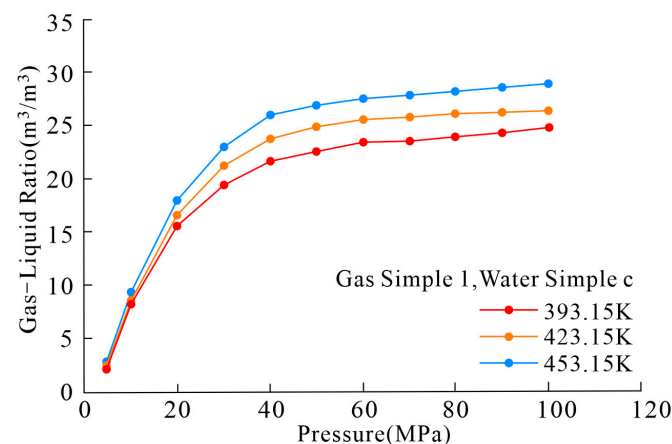


Figure 2. The solubility of natural gas in formation salt water varies with pressure and temperature.

3.2. Influence of Salinity on Natural Gas Solubility

Figure 3 shows the variation pattern of natural gas solubility with increasing formation water salinity at a constant temperature of 393.15 K. The curves clearly indicate a significant negative correlation between the two. The main mechanism causing this phenomenon is the “salting-out effect” induced by dissolved salts in the water. Specifically, the addition of salt ions inhibits gas dissolution in two ways: Firstly, inorganic salts reduce the activity coefficient of water, thereby weakening its capacity as a solvent to accommodate gas molecules. Secondly, salt ions undergo hydration in aqueous solutions, forming complex hydrated ions. This process “captures” or “binds” a large number of originally available free water molecules, producing a so-called “solvent effect.” Under the combined action of these two mechanisms, the dissolution process of natural gas in formation water is significantly inhibited as salinity increases, leading to a decrease in solubility.

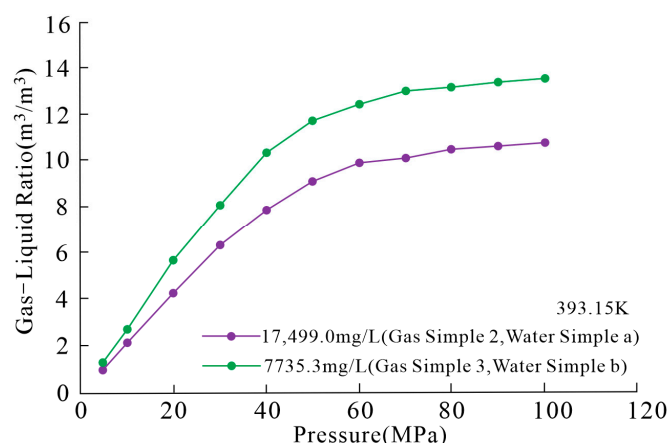


Figure 3. Diagram of natural gas dissolution with pressure in saltwater systems with different salt contents.

3.3. Influence of Different CO₂ Content on Natural Gas Solubility

As shown in Figure 4, under the condition of 393.15 K, natural gas solubility is closely related to the CO₂ content in the system. This primarily stems from the unique dissolution behavior of CO₂ itself: its solubility in formation water decreases with increasing temperature but increases significantly with rising pressure. Moreover, its solubility value far exceeds that of methane under the same temperature and pressure conditions. This result directly confirms that CO₂ possesses stronger dissolution capacity and affinity in formation water compared to methane.

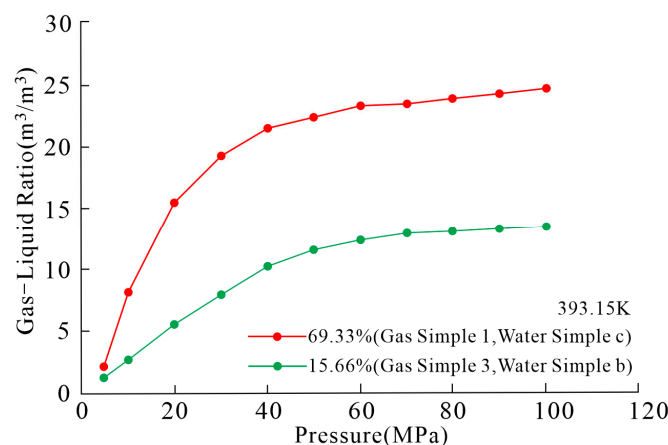


Figure 4. The solubility of natural gas in formation saltwater varies with pressure under different CO₂ contents.

4. Theoretical Model

Based on the equations of state and mixed-solution (solubility) methods adopted in previously established gas solubility models, and given that a gas mixture solubility model requires an equation of state with appropriate mixing rules, virial-type and multi-parameter equations of state are difficult to satisfy. Most studies therefore adopt cubic equations. However, cubic equation-based models, such as the Zirrahi model, have a limited pressure range for solubility calculation (not exceeding 60 MPa) and exhibit relative errors of 2.57–20.25%, making them difficult to apply under ultra-high-temperature and high-pressure formation conditions. Therefore, the equation of state based on the Helmholtz free energy (Mao et al., 2017; Duan and Mao, 2006; Mao et al., 2006) [23,55,56] was adopted to evaluate and calculate the solubility of high-temperature, high-pressure, high-CO₂ gas in the South China Sea, as shown in Equation (4).

$$\ln m_i = \ln \gamma_i P + \ln \varphi_i - \frac{\mu_i^{L(0)}}{RT} - \sum_c 2\lambda_{i-c} m_c - \sum_a 2\lambda_{i-a} m_a - \sum_c \sum_a \xi_{i-c-a} m_c m_a \quad (4)$$

where m_i is the solubility of component i in the liquid phase (mol/kg); γ_i is the activity coefficient of component i in the liquid phase; P is pressure (bar); φ_i is the fugacity coefficient of component i ; $\mu_i^{L(0)}$ is the standard chemical potential of gas component i in the liquid phase, the chemical potential when component i solubility is 1 mol/kg and activity coefficient is 1 in an ideal solution; λ , ξ are binary and ternary interaction coefficients, respectively; c and a represent cations and anions, respectively; $\frac{\mu_i^{L(0)}}{RT}$, λ , ξ are all functions of temperature and pressure. To simplify parameters, λ_{i-CL} is set to 0. Other specific parameters can be obtained by fitting experimental solubility data for CH₄, CO₂, C₂H₆, and C₃H₈ in pure water and salt solutions. Mao and Duan et al. [55,56] have previously determined the standard chemical potentials for pure CO₂, CH₄, and N₂, as well as the binary and ternary interaction parameters between these gases and sodium and chloride ions. Table 5 lists the relevant interaction parameters for CO₂, CH₄, and N₂.

Table 5. Relevant interaction parameters for CO₂, CH₄, and N₂.

T-P Coefficient		μ/RT	λ_{i-Na^+}	$\xi_{i-Na^+-Cl^-}$
CH ₄	C ₁	8.314	-8.122×10^{-1}	-2.990×10^{-3}
	C ₂	-7.277×10^{-4}	1.063×10^{-3}	
	C ₃	2.148×10^3	1.889×10^2	
	C ₄	-1.401×10^{-5}		
	C ₅	-6.674×10^5		
	C ₆	7.698×10^{-3}	4.410×10^{-5}	
	C ₇	-5.025×10^{-6}		
	C ₈	-3.009		
	C ₉	4.846×10^2		
	C ₁₀		-4.679×10^{-11}	
CO ₂	C ₁	28.944	-4.113×10^{-1}	3.363×10^{-4}
	C ₂	-3.545×10^{-2}	6.076×10^{-4}	-1.982×10^{-5}
	C ₃	-4.770×10^3	9.753×10	
	C ₄	1.027×10^{-5}		
	C ₅	33.812		
	C ₆	9.040×10^{-3}		
	C ₇	-1.149×10^{-3}		
	C ₈	-0.307	-2.376×10^{-2}	2.122×10^{-3}
	C ₉	-9.073×10^{-2}	1.706×10^{-2}	-5.248×10^{-3}
	C ₁₀	9.327×10^{-4}		
	C ₁₁		1.413×10^{-5}	

Table 5. Cont.

T-P Coefficient	μ/RT	λ_{i-Na^+}	$\xi_{i-Na^+-CL^-}$
N ₂	C ₁	-2.309×10	-2.443
	C ₂	5.604×10^{-2}	3.635×10^{-3}
	C ₃	9.880×10^3	4.474×10^2
	C ₄	-5.109×10^{-5}	
	C ₅	-1.322×10^6	
	C ₆	-4.954×10^{-4}	-1.371×10^{-5}
	C ₇	1.269×10^{-6}	
	C ₈	5.141×10^{-1}	
	C ₉	-6.473×10^{-5}	7.103×10^{-6}

Therefore, by calculating component fugacity using the Helmholtz free energy equation of state, combining it with the Pitzer electrolyte activity coefficient model to calculate solution activity, solubility is computed according to the gas–liquid phase equilibrium theoretical relationship.

4.1. Model Validation

To systematically evaluate the accuracy and reliability of this model, natural gas and formation water from a high-temperature, high-pressure gas field in the western South China Sea were selected. Experiments simulating different temperature and pressure conditions, different gas compositions, and detection of dissolved gas–liquid ratios were conducted. The mixed model based on Helmholtz free energy was used to fit the experimental data from this study.

- (1) Fitting results for layer A, the basic data for this layer are shown in Table 6, and the experimental result fitting is shown in Figure 5.

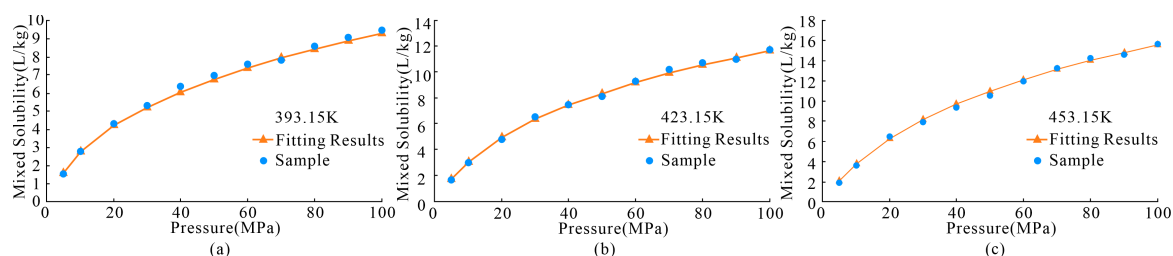


Figure 5. Fitting results for layer A. (a) Fitting results of 393.15 K; (b) fitting results of 423.15 K; (c) fitting results of 453.15 K.

Table 6. Basic parameters.

Component	Layer A	Layer B	Layer C
N ₂	3.02%	2.34%	2.45%
CO ₂	11.42%	15.66%	68.97%
C ₁	75.99%	77.04%	28.58%
C ₂	7.10%	4.95%	0.00%
C ₃	1.28%	0.00%	0.00%
Na ⁺	0.282600 mol/L	0.142020 mol/L	0.169000 mol/L
K ⁺	0.018880 mol/L	0.016677 mol/L	0.020605 mol/L
Ca ²⁺	0.002500 mol/L	0.001500 mol/L	0.000753 mol/L
Mg ²⁺	0.000000 mol/L	0.000000 mol/L	0.000000 mol/L
CL ⁻	0.200366 mol/L	0.097490 mol/L	0.101676 mol/L
SO ₄ ²⁻	0.021476 mol/L	0.003099 mol/L	0.003398 mol/L

- (2) Fitting results for layer B; the basic data for this layer are shown in Table 6, and the experimental result fitting is shown in Figure 6.

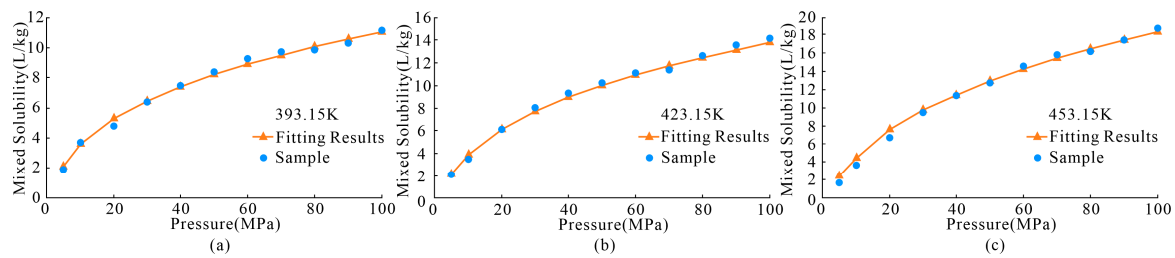


Figure 6. Fitting results for layer B. (a) Fitting results of 393.15 K; (b) fitting results of 423.15 K; (c) fitting results of 453.15 K.

- (3) Fitting results for layer C; the basic data for this layer are shown in Table 6, and the experimental result fitting is shown in Figure 7.

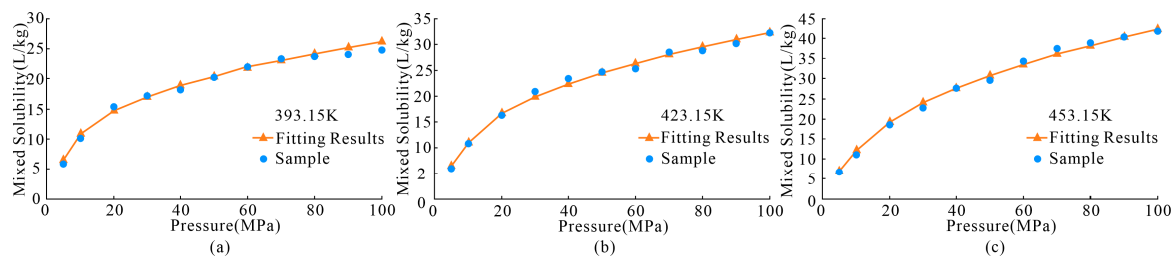


Figure 7. Fitting results for layer C. (a) Fitting results of 393.15 K; (b) fitting results of 423.15 K; (c) fitting results of 453.15 K.

4.2. Model Application

By comparing the model's calculated values with experimental data, the error range between experimental data and calculated values is within 0–10%, indicating that this model provides a good description of mixed gas solubility in aqueous solutions.

Using the natural gas solubility model under high-temperature and high-pressure conditions, the gas–water solubility (converted to standard conditions) of four field wells at different formations was calculated under formation pressure and temperature conditions in the study area. Subsequently, the actual dissolved gas volume in the formation was calculated based on the gas–water ratio to evaluate the gas–water state under formation conditions. As shown in Table 7, the field gas production rate is significantly higher than the dissolved gas volume under formation conditions. Therefore, under reservoir conditions, the gas exists mainly as free gas, indicating exploration potential.

Table 7. Relevant data from formation testing.

Well	Formation Pressure (MPa)	Formation Temperature (K)	Water Production Rate (m ³ /d)	Gas Production Rate (m ³ /d)	Field Gas–Water Ratio (m ³ /m ³)	Calculated Gas–Water Ratio at Standard Condition (m ³ /m ³)	Calculated Solution Gas Rate at Standard Condition (m ³ /d)
L7	92.29	473.15	153.1	38,819	253.55	20	3062
	92.29	473.15	194.4	59,684	307	20	3888
	92.29	473.15	244.8	73,023	298.2	20	4896
L8	91.941	473.15	282	22,295	79	36.3	10,236.6
	91.941	473.15	190	14,269	75.1	36.3	6897
	91.941	473.15	254.4	17,222	67.8	36.3	9234.72
L9	88.5	468.45	13.53	8109	599	33.2	449.196
	88.5	468.45	7.7	3618	469	33.2	255.64
	88.5	468.45	15.3	7529	492	33.2	507.96
L10	91	462.75	1.04	50,384	48,446	41.7	43.368

5. Conclusions

This study systematically investigates the effects of temperature, pressure, salinity, and CO₂ content on the solubility of natural gas in formation water through a combination of high-temperature and high-pressure experiments and theoretical modeling. A high-precision solubility prediction model suitable for high-temperature, high-pressure, and high-CO₂ natural gas systems was selected. The main conclusions are as follows:

- (1) Through experimental methods, solubility experiments of different gases in various formation waters were conducted, and the effects of temperature (393.15–453.15 K), pressure (5–100 MPa), CO₂ content (5–75%), and salinity (7735.3–17,499.0 mg/L) on solubility were obtained. At constant temperature, the solubility of natural gas in water shows a significantly positive correlation with pressure. In the low-pressure range, solubility increases sharply with increasing pressure, indicating high dissolution efficiency. When the pressure exceeds a certain critical value, the increasing trend of solubility slows down significantly and eventually levels off. Under constant temperature and pressure, as salinity increases from 7735.3 mg/L to 17,499.0 mg/L, solubility decreases, showing a significantly negative correlation. Moreover, under high-pressure conditions, the effect of salinity on gas solubility in water becomes more pronounced. Under the same temperature and pressure conditions, the solubility of CO₂ is much higher than that of alkane gases.
- (2) Based on big data analysis and computation, a natural gas solubility model suitable for high-temperature, high-pressure, and high-CO₂ conditions in the western South China Sea was established using the dimensionless Helmholtz free energy equation of state combined with the Pitzer electrolyte activity coefficient model. The overall relative error between the model-calculated values and experimental data is less than 10%.

Author Contributions: Conceptualization, S.C. and H.L.; methodology, S.C. and H.L.; software, S.C.; validation, H.L., J.K. and Q.W.; formal analysis, S.C.; investigation, Z.D.; resources, S.C. and Q.W.; data curation, Z.D.; writing—original draft preparation, H.L. and J.K.; writing—review and editing, K.X.; visualization, Z.D.; supervision, S.C. and Q.W.; project administration, S.C.; funding acquisition, S.C. and Q.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Guangdong Provincial University Innovation Team focused on Oil and Gas Resources, (Project No. 2022KCXTD018).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: Authors Shuheng Cui, Hao Liang, and Jie Kong were employed by the company CNOOC Energy Development Co., Ltd., Engineering Technology Company, Zhanjiang, China. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

References

1. Zhai, P.; Chen, H. Discharging Zones of Overpressure System in Qiongdongnan Basin, Northern South China Sea: Implications for Favorable Sites of Natural Gas Accumulation. *J. Earth Sci. (J. China Univ. Geosci.)* **2013**, *38*, 832–842.
2. Millero, F.J. Thermodynamics of the carbon dioxide system in the oceans. *Geochim. Cosmochim. Acta* **1995**, *59*, 661–677. [[CrossRef](#)]
3. Karakatsani, K.E.; Kontogeorgis, M.G. Thermodynamic Modeling of Natural Gas Systems Containing Water. *Ind. Eng. Chem. Res.* **2013**, *52*, 3499–3513. [[CrossRef](#)]
4. Mohammadi, A.H.; Chapoy, A.; Tohidi, B.; Richon, D. Gas solubility: A key to estimating the water content of natural gases. *Ind. Eng. Chem. Res.* **2006**, *45*, 4825–4829. [[CrossRef](#)]
5. Yang, Y.; Dai, H.M.; Huang, D.; Zhou, Z.; Wang, X. New understandings of gas pooling conditions in Wuzhishan structure, the Sichuan Basin. *Nat. Gas Ind.* **2008**, *28*, 65–68.
6. Xiang, X.; Li, W.; Chen, J. Exsolution mechanism and gas-accumulation feature in shallow-middle depths in Jiyang Depression. *Geol. Sci. Technol. Inf.* **2006**, *25*, 57–60.

7. Hao, S.; Zhang, Z. The characteristic of the solubility of natural gas in formation waters and it's geological significance. *Acta Pet. Sin.* **1993**, *14*, 12–22.
8. Fu, X.T.; Wang, Z.P.; Lu, S.F.; Zhu, X.H. Mechanism of natural gas dissolving in brines and the dissolving equation. *Acta Pet. Sin.* **2000**, *21*, 89–94.
9. Cui, S.; Wu, Q.; Wang, Z. Estimating the Influencing Factors of Gas–Water Relative Permeability in Condensate Gas Reservoirs under High-Temperature and High-Pressure Conditions. *Processes* **2024**, *12*, 728. [[CrossRef](#)]
10. Cui, S.; Wang, J.; Kong, J.; Guo, M.; Mou, Z.; Ma, J.; Chen, X.; Wu, Q. An experimental investigation into carbon dioxide flooding and rock dissolution in low-permeability reservoirs of the South China Sea. *Open Geosci.* **2025**, *17*, 20250818. [[CrossRef](#)]
11. Cai, W.; Gao, L.; Wang, Z.; Duan, X.; Bian, J.; Hua, Y.; Che, X. A new method for calculating the solubility of carbon dioxide in liquefied natural gas. *Nat. Gas Ind.* **2023**, *43*, 108–116.
12. Yang, P.J.; Peng, S.; Wang, J.; Wang, Q.; Ren, N.; Song, W. Carbon Capture, Utilization and Storage (CCUS) technology development status and application prospects. *China Environ. Sci.* **2024**, *44*, 404–416.
13. Li, X.; Zhang, Y.; Chen, Z.; Li, G.; Tang, L.; Yan, K. Equilibrium Dissociation Conditions for Gas Hydrate in Porous Media Using Two Models. *Acta Chim. Sin.* **2007**, *65*, 2187–2196.
14. Dubessy, J.; Tarantola, A.; Sterpenich, J. Modelling of liquid-vapour equilibria in the H₂O–CO₂–NaCl and H₂O–H₂S–NaCl systems to 270 °C. *Oil Gas Sci. Technol.-Rev. l'IFP* **2005**, *60*, 339–355. [[CrossRef](#)]
15. Sevestre, C.; Chabab, S.; Brocus, J.; Coquelet, C. Modeling of thermodynamic properties of H₂ and H₂ mixtures using a three-parameter cubic equation of state. *Int. J. Hydrogen Energy* **2025**, *101*, 1029–1043. [[CrossRef](#)]
16. Zhao, W.; Li, W.; Sun, X.; Cao, X.; Xiang, S. Research and evaluation on generalized alpha functions based on PR EoS. *CIESC J.* **2020**, *71*, 1234–1245.
17. Guo, T.; Hu, J.W.; Wang, X.H.; Jin, L.H.; Wang, Y.Z. Thermodynamic modeling of supercritical water: A cubic equation of state up to 4273K and 2GPa. *Acta Petrol. Sin.* **2016**, *32*, 2196–2208.
18. Andreas, J.; Cornelia, B.; Markus, R. The Representation of Cross Second Virial Coefficients by Multifluid Mixture Models and Other Equations of State. *Ind. Eng. Chem. Res.* **2021**, *60*, 9286–9295. [[CrossRef](#)]
19. Gokul, N.; Schultz, A.J.; Kofke, D.A. Properties of supercritical N₂, O₂, CO₂, and NH₃ mixtures from the virial equation of state. *AIChE J.* **2021**, *67*, e17072.
20. Sadus, R.J. Intermolecular Potential-Based Equations of State from Molecular Simulation and Second Virial Coefficient Properties. *J. Phys. Chem. B* **2018**, *122*, 7757–7763. [[CrossRef](#)] [[PubMed](#)]
21. Niu, L.; Kaur, I.; Yadav, A.; Sead, F.F.; Shahriari, R. Prediction of CO₂ solubility in polar aprotic solvents using the PC-SAFT equation of state. *J. Supercrit. Fluids* **2025**, *221*, 106575. [[CrossRef](#)]
22. Pang, Y.; Ding, Z. Modeling CO₂ solubility in imidazolium-based ionic liquids with extended PC-SAFT equation of state. *Sep. Purif. Technol.* **2025**, *360*, 130983. [[CrossRef](#)]
23. Mao, S.; Lü, M.; Shi, Z. Prediction of the PVTx and VLE properties of natural gases with a general Helmholtz equation of state. Part I: Application to the CH₄–C₂H₆–C₃H₈–CO₂–N₂ system. *Geochim. Cosmochim. Acta* **2017**, *219*, 74–95. [[CrossRef](#)]
24. Hossein, S. Modeling the Solubility of Hydrogen Sulfide in Ionic Liquids Using van der Waals Equation of State. *Theor. Found. Chem. Eng.* **2021**, *54*, 1276–1289.
25. Saali, A.; Hossein, S.; Mohammad, S. Modeling the Solubility of Carbon Dioxide and 1,1,1,2-Tetrafluoroethane in Ionic Liquids Using the van der Waals and Generic Redlich-Kwong Equations of State. *Theor. Found. Chem. Eng.* **2021**, *55*, 129–139. [[CrossRef](#)]
26. Ratnawati, R. Van Der Waals Mixing Rules for The Redlich-Kwong Equation of State. Application For Supercritical Solubility Modeling. *Reaktor* **2012**, *10*, 96–102.
27. Soave, G. Improvement of the van der Waals equation of state. *Chem. Eng. Sci.* **1984**, *39*, 357–369. [[CrossRef](#)]
28. Lin, C.T.; Daubert, T.E. Prediction of partial molar volume from the Lee-Kesler equation of state. *Aiche J.* **1979**, *25*, 365–367. [[CrossRef](#)]
29. Lin, C.T.; Daubert, T.E. Estimation of Partial Molar Volume and Fugacity Coefficient of Components in Mixtures from the Soave and Peng-Robinson Equations of State. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 51–59. [[CrossRef](#)]
30. Bacsik, Z.; Lopes, J.N.C.; Gomes, M.F.C.; Jancsó, G.; Mink, J.; Pádua, A.A.H. Solubility isotope effects in aqueous solutions of methane. *J. Chem. Phys.* **2002**, *116*, 10816–10824. [[CrossRef](#)]
31. Hou, S.-X.; Maitland, G.C.; Trusler, J.M. Measurement and modeling of the phase behavior of the (carbon dioxide + water) mixture at temperatures from 298.15 K to 448.15 K. *J. Supercrit. Fluids* **2013**, *73*, 87–96. [[CrossRef](#)]
32. Forte, E.; Galindo, A.; Trusler, J.P.M. Experimental and molecular modeling study of the three-phase behavior of (*n*-Decane + carbon dioxide + water) at reservoir conditions. *J. Phys. Chem. B* **2011**, *115*, 14591–14609. [[CrossRef](#)] [[PubMed](#)]
33. Kedge, C.; Trebble, M. Improvements to a new equation of state for pure components. *Fluid Phase Equilibria* **2004**, *217*, 257–262. [[CrossRef](#)]
34. Huang, H.; Sandler, S.I. Prediction of vapor-liquid equilibria at high pressures using activity coefficient parameters obtained from low-pressure data: A comparison of two equation of state mixing rules. *Ind. Eng. Chem. Res.* **1993**, *32*, 1498–1503. [[CrossRef](#)]

35. Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260. [\[CrossRef\]](#)
36. Kunz, O. The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures. *J. Chem. Eng. Data* **2007**, *57*, 3032–3091.
37. Xiang, S.G.; Zhao, F.L.; Sun, X.Y.; Zhao, W.Y.; Chen, Y.S. Research progress in solid-liquid equilibrium calculation. *J. Qingdao Univ. Sci. Technol. (Nat. Sci. Ed.)* **2023**, *44*, 26–37.
38. Han, X.; Wang, Q.; Chen, G. The Vapor Liquid Equilibrium Mixing Rules Based On Excess Free Energy Models. *Chem. Bull.* **2006**, *69*, 95–103.
39. Adler, S.B.; Friend, L.; Pigford, R.L. Application of the Wohl equation to ternary liquid-vapor equilibria. *AIChE J.* **1966**, *12*, 629–637. [\[CrossRef\]](#)
40. Mato, F.; Mato, F.A. Two-parameter model for correlating liquid phase activity coefficients of binary systems. *Fluid Phase Equilibria* **1985**, *20*, 183–188. [\[CrossRef\]](#)
41. Mao, Y.; Yang, Z.; Guo, H.; Chen, Y.; Mo, S.; Luo, X.; Chen, J.; Liang, Y. The Thermodynamic Properties of Non-Associating and Associating Fluids: A Systematic Evaluation of SAFT-Type Equations of State. *Int. J. Thermophys.* **2023**, *44*, 32. [\[CrossRef\]](#)
42. Wu, H.; Wang, L.; Zhang, H.; Wu, C.; Han, J.; Wang, Z.; Li, M. Application of the perturbed-chain statistical associating fluid theory to predicting drug-polymer miscibility and stability in amorphous solid dispersions: A comprehensive overview. *Front. Chem. Sci. Eng.* **2025**, *19*, 117. [\[CrossRef\]](#)
43. Rowane, A.J.; Menegazzo, D.; Bell, I.H. Modeling the Vapor–Liquid Equilibria of Sustainable Aviation Fuel Components with Nitrogen Using the PC-SAFT Equation of State. *J. Chem. Eng. Data* **2024**, *70*, 370–387. [\[CrossRef\]](#)
44. Li, K.; Ye, Z.; Liang, X. PC-SAFT-Type Equations of State Revisited: Quantifying the Value of Base Model Adjustments through Universal Criteria Benchmarks. *Ind. Eng. Chem. Res.* **2025**, *64*, 16873–16888. [\[CrossRef\]](#)
45. Walker, P.J.; Mueller, S.; Smirnova, I. Confidence-Interval and Uncertainty-Propagation Analysis of SAFT-type Equations of State. *J. Chem. Eng. Data* **2023**, *69*, 495–508. [\[CrossRef\]](#)
46. Zirrahi, M.; Azin, R.; Hassanzadeh, H.; Moshfeghian, M. Mutual solubility of CH₄, CO₂, H₂S, and their mixtures in brine under subsurface disposal conditions. *Fluid Phase Equilibria* **2012**, *324*, 80–93. [\[CrossRef\]](#)
47. Ziabakhsh-Ganji, Z.; Kooi, H. An Equation of State for thermodynamic equilibrium of gas mixtures and brines to allow simulation of the effects of impurities in subsurface CO₂ storage. *Int. J. Greenh. Gas Control.* **2012**, *11*, 21–34. [\[CrossRef\]](#)
48. Prausnitz, J.M.; Lichtenthaler, R.N.; De Azevedo, E.G. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Pearson Education: London, UK, 1998.
49. Li, H.; Yan, J. Impacts of equations of state (EOS) and impurities on the volume calculation of CO₂ mixtures in the applications of CO₂ capture and storage (CCS) processes. *Appl. Energy* **2009**, *86*, 2760–2770. [\[CrossRef\]](#)
50. Li, H.; Yan, J. Evaluating cubic equations of state for calculation of vapor–liquid equilibrium of CO₂ and CO₂-mixtures for CO₂ capture and storage processes. *Appl. Energy* **2008**, *86*, 826–836.
51. Haji, M.; Corvisier, J.; Ahmar, E.E.; Coquelet, C. Impact of impurities on CO₂ storage in saline aquifers: Modelling of gases solubility in water. *Int. J. Greenh. Gas Control.* **2018**, *68*, 247–255. [\[CrossRef\]](#)
52. Corvisier, J.; Bonvalot, A.; Lagneau, V.; Chiquet, P.; Renard, S.; Sterpenich, J.; Pironon, J. Impact of Co-injected Gases on CO₂ Storage Sites: Geochemical Modeling of Experimental Results. *Energy Procedia* **2013**, *37*, 3699–3710. [\[CrossRef\]](#)
53. Hassanpouryouzband, A.; Farahani, V.M.; Yang, J.; Tohidi, B.; Chuvilin, E.; Istomin, V.; Bukhanov, B.A. Solubility of Flue Gas or Carbon Dioxide–Nitrogen Gas Mixtures in Water and Aqueous Solutions of Salts: Experimental Measurement and Thermodynamic Modeling. *Ind. Eng. Chem. Res.* **2019**, *58*, 3377–3394. [\[CrossRef\]](#)
54. GB/T 26981-2020; Analysis Method for Reservoir Fluid Physical Properties. China Standards Press: Beijing, China, 2020.
55. Duan, Z.; Mao, S. A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523 K and from 1 to 2000 bar. *Geochim. Cosmochim. Acta* **2006**, *70*, 3369–3386. [\[CrossRef\]](#)
56. Mao, S.; Duan, Z. A thermodynamic model for calculating nitrogen solubility, gas phase composition and density of the N₂–H₂O–NaCl system. *Fluid Phase Equilibria* **2006**, *248*, 103–114. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.