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# Integrated Thermodynamic and Kinetic Modeling of Methane Hydrate Formation: Experimental Validation and Predictive Analysis

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# Комплексное термодинамическое и кинетическое моделирование образования гидрата метана: экспериментальная проверка и прогнозный анализ

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Hydrate, Methane, Thermodynamic model, kinetic model, Formation, Dissociation, Temperature, Pressure, Gas field, pipeline, Van der Waals-Platteeuw, Fluid Theory

Gas hydrate formation presents significant flow assurance challenges in oil and gas operations, particularly in subsea pipelines where low temperatures (<290 K) and high pressures (>5 MPa) create ideal conditions for crystallization. This study integrates experimental and modeling approaches to characterize methane hydrate phase equilibria, the primary component of natural gas hydrates. Controlled stepwise heating experiments (0.3–1 K/hr) in a high-pressure reactor (50–130 bar range) precisely determined dissociation conditions with temperature uncertainty of ±0.1 K and pressure accuracy of ±0.05 MPa. A novel thermodynamic framework combining the PC-SAFT equation of state for chain molecule interactions, the CPA equation for hydrogen bonding effects, and Van der Waals-Platteeuw hydrate theory demonstrated exceptional predictive capability across the 280–290 K and 5.5–13 MPa operating window. The model's robustness was validated against four independent experimental datasets, achieving average absolute deviations of 1.55% for pressure and 0.05 % for temperature with the CPA approach, outperforming PC-SAFT in high-pressure regimes.
The study also investigated kinetic behavior using two experimental methods, with Method B (post-cooling gas injection) providing unambiguous induction time measurements. Results revealed critical insights into hydrate nucleation and dissociation dynamics, including the identification of equilibrium points at the intersection of heating-cooling curves. These findings advance fundamental understanding of hydrate thermodynamics while offering practical tools for pipeline design, operational optimization, and emergency response planning in Arctic and deepwater environments. The developed methodology bridges the gap between laboratory-scale data and field-scale applications, ensuring accurate hydrate stability predictions under industrial conditions.

*Ключевые слова:*
гидрат, метан, термодинамическая модель, кинетическая модель, формирование, диссоциация, температура, давление, газовое месторождение, трубопровод, Ван-дер-Ваальс-Платтеу, теория жидкостей.

Образование газовых гидратов создает значительную проблему обеспечения непрерывного потока при добыче нефти и газа, особенно в подводных трубопроводах, где низкие температуры (<290 К) и высокое давление (>5 МПа) создают идеальные условия для их кристаллизации. В исследовании используются экспериментальные и модельные подходы для определения фазового равновесия гидрата метана, основного компонента гидратов природного газа. Контролируемые эксперименты по ступенчатому нагреву (0,3–1 К/ч) в реакторе высокого давления (в диапазоне 50–130 бар) позволили точно определить условия диссоциации с погрешностью температуры ± 0,1 К и точностью давления ± 0,05 МПа. Новая термодинамическая модель, объединяющая уравнение состояния статистической теории ассоциированной жидкости для взаимодействия молекул в цепочке, уравнение кубической ассоциации для учета эффектов водородных связей и теорию гидратов Ван-дер-Ваальса – Платтеу, продемонстрировала исключительную прогностическую способность в диапазоне 280–290 К и 5,5–13 МПа. Ровность модели была подтверждена четырьмя независимыми экспериментальными наборами данных, при этом среднее абсолютное отклонение составило 1,55 % для давления и 0,05 % для температуры при использовании подхода из уравнения кубической ассоциации, что превосходит уравнение состояния статистической теории ассоциированной жидкости в режимах высокого давления.
В ходе исследования также изучалось кинетическое поведение с использованием двух экспериментальных методов, при этом метод Б (закачка газа после охлаждения) обеспечивал однозначные измерения времени индукции. Результаты позволили получить важные сведения о динамике образования и диссоциации гидратов, в том числе об определении точек равновесия на пересечении кривых нагрева и охлаждения. Эти результаты способствуют фундаментальному пониманию термодинамики гидратов и предлагают практические инструменты для проектирования трубопроводов, оптимизации эксплуатации и планирования действий в чрезвычайных ситуациях в арктических и глубоководных условиях. Разработанная методология устраняет разрыв между данными лабораторных исследований и практическим применением в полевых условиях, обеспечивая точный прогноз стабильности гидратов в промышленных условиях.

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## Introduction

Gas hydrates, crystalline compounds formed when gas molecules are trapped within a lattice of water molecules under specific temperature and pressure conditions, pose significant operational challenges in the oil and gas industry. Among these, methane hydrate – the primary constituent of natural gas hydrates – is particularly problematic in pipelines and subsea equipment, where low temperatures and high pressures create ideal conditions for its formation [1, 2]. The resulting blockages can lead to severe flow assurance issues, safety hazards, and substantial economic losses.

Historically, hydrate research has evolved from early observations by Sir Humphry Davy in 1810 to modern thermodynamic and kinetic modeling [3-4]. While empirical methods have provided foundational insights, the complexity of hydrate [5] behavior necessitates advanced predictive models to ensure accurate phase equilibrium calculations. Current challenges include the need for precise determination of hydrate stability zones and the development of mitigation strategies that align with environmental and operational constraints.

This study focuses on the equilibrium conditions of methane hydrate formation in pure water systems, employing a stepwise heating method to experimentally determine phase boundaries [6–8].

In this research, the thermodynamic conditions of methane hydrate dissociation were obtained by laboratory tests using the step heating method, and then the obtained results were compared and evaluated with the experimental data of other researchers in the published articles. To develop a suitable kinetic model that can predict the induction time of gas hydrate formation, it is necessary to first calculate the driving force of the kinetic model (difference). between hydrate formation and equilibrium fugacity) using a suitable thermodynamic model. When designing hydrate-related processes, the first problem is predicting the temperature and pressure at which the hydrate will form. So far, various methods have been described to predict the conditions of hydrate formation. These methods can be divided into two general categories: (1) experimental methods (manual methods) and (2) thermodynamic models (computer methods). All the studies conducted in the field of predicting the conditions of hydrate crystal formation have been based on the science of chemical thermodynamics. A novel thermodynamic model, integrating the PC-SAFT and CPA equations of state, is developed to predict fugacity-driven hydrate formation. By validating results against existing literature, this work aims to enhance predictive accuracy and support industrial applications in hydrate prevention.

The findings contribute to a deeper understanding of hydrate thermodynamics while offering practical tools for optimizing gas transport and storage in hydrate-prone environments.

## Research method and laboratory studies

The outline of the laboratory system used in the current study to conduct thermodynamic studies of phase balance as well as kinetic investigations of hydrate formation by measuring the induction time is shown in Figure (1). The main part of the device is a cylindrical reactor with an effective internal capacity of 100 ± 0.5 cubic centimeters (with an internal diameter of 5.5 centimeters and a height of 4.2 centimeters), which can withstand a maximum pressure of 20 MPa. This reactor is equipped with a six-blade magnetic stirrer (diameter 3.3 cm) to ensure effective contact between the fluid and the hydrate crystals. It should be noted that the stirring speed can be adjusted by separate

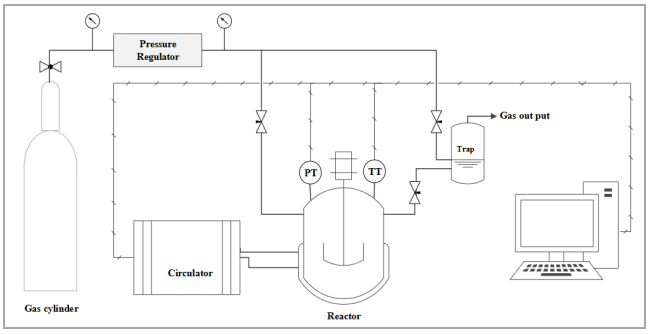



Fig. 1. Schematic of the test system used

system. A platinum resistance thermometer (Pt-100) with a valid calibration of less than 0.1 K was used in the liquid phase to measure the temperature of the internal contents of the reactor. Also, a pressure transducer has been used to monitor the system pressure with a standard calibration of less than 5 kPa. Also, a programmable heating/cooling device with an accuracy of 0.1 k (Lauda model) containing a mixture of water and ethylene glycol as a coolant was used to adjust the temperature of the reactor. This system is also equipped with a data collection and recording system with special software so that it can receive and store the temperature and pressure of the cell at regular intervals.

There are different methods for determining hydrate equilibrium points. In this research, the Laboratory research of the methane hydrate system is carried out using the step-by-step heating method in the constant volume system in order to determine the equilibrium points of the hydrate [9].

The thermodynamic testing protocol followed these steps:

System Preparation: Thoroughly cleaned and dried test cell (100 $cm^3$ effective volume); Charged with distilled water (60 % of total cell volume); Evacuated and purged with test gas (99.99 % purity methane) to remove residual air.

Initial Conditions: Pressurized to target pressure (50–130 bar range); Stabilized at 313.15 K for 60 minutes to ensure equilibrium.

Hydrate Formation: Cooled at 1 K/h to 278 K; Monitored for hydrate formation indicators: Pressure drop (gas consumption) and Temperature spike (exothermic formation); Allowed 3–5 hours for complete crystallization.

Applied controlled heating protocol: Initial heating at 0.5 K/h near equilibrium zone; Stepwise heating at 0.3 K/h with 3–6 hour isothermal holds; Recorded P-T data every 20 seconds; Determined equilibrium at heating-cooling curve intersection.

## The method of conducting kinetic experiments

Two experimental approaches were employed to determine hydrate nucleation induction times:

1. Method A (Pre-pressurization):
   - Load distilled water into reactor.
   - Inject test gas at initial pressure.
   - Cool system to target temperature at maximum cooling rate (1 K/h).
2. Method B (Post-cooling):
   - Cool reactor to target temperature first.
   - Then inject test gas.
   - Record induction time from gas injection to first hydrate detection.

Method B was adopted as the standard approach because:

- Eliminates cooling path dependence.
- Provides unambiguous $t = 0$ for induction time measurement.
- Removes cooling rate as a variable.

Monitoring Parameters:
- Detection criteria:
  - Characteristic temperature increase (exothermic nucleation).
  - Simultaneous pressure drop (gas consumption).
- Data acquisition:
  - Continuous P-T recording (20 sec intervals).
  - Measurement uncertainties:
    - Temperature: ± 0.1 K.
    - Pressure: ± 0.05 MPa.

### Theoretical calculations and modeling – thermodynamic calculations of hydrate formation/dissociation

We employed two advanced equations of state to model hydrate phase equilibria:

1. Theoretical Framework

PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory): Accounts for chain connectivity and association effects. CPA (Cubic Plus Association): Combines SRK cubic equation with association term. Both models explicitly treat hydrogen bonding interactions. Demonstrated superior accuracy to cubic EOS when using binary interaction parameters (kij) [10].

2. Model Implementation [11]

Applied van der Waals-Platteeuw theory for hydrate phase fugacity. Calculated water/gas phase fugacity using both PC-SAFT and CPA. Optimized $k_{ij}$ parameters using methane solubility data. Validated against experimental hydrate dissociation conditions

3. Thermodynamic Basis
4. Hydrate formation occurs when:

- Hydrate phase exhibits lower chemical potential than liquid water/ice
- Water molecules undergo two-stage transition:

1. Formation of empty hydrate lattice.
2. Occupation by guest molecules.

According to the Van der Waals-Platteeuw thermodynamic model, equilibrium conditions for hydrate formation occur when the chemical potential of water in the hydrate phase ($\mu_W^H$) equals that in the bulk liquid water phase ($\mu_W^L$), as expressed in Equation (1):

$$\mu_W^H = \mu_W^L. \quad (1)$$

The three-phase equilibrium conditions for the gas-hydrate-liquid water system (G-H-WL) are determined by thermodynamic equilibrium criteria, requiring equality of component fugacities across all coexisting phases. This necessitates:

$$f_w^L = f_w^H, \quad (2)$$

where $f_w^L$ and $f f_w^H$ represent the fugacity of water in the liquid and hydrate phases, respectively. This condition, coupled with analogous fugacity equalities for other components, fully constrains the equilibrium state of the system at given temperature and pressure conditions.

Van der Waals and Platteeuw quantified the thermodynamic effect of guest molecule occupation on hydrate stability through a Langmuir adsorption framework. The chemical potential difference between water in the empty hydrate lattice ($\mu_w^{MT}$) and the gas-filled hydrate phase ($\mu_w^H$) is given by:

$$\frac{\mu_w^H - \mu_w^{MT}}{RT} = -\sum_{i=1}^{N_{cavity}} \nu_i \left(1 - \sum_{j=1}^{NH} Y_{ij}\right), \quad (3)$$

where $\nu_i$ – number of type-i cavities per water molecule; $Y_{ij}$ – fractional occupancy of cavity type i by gas component *j*; *NH* – number of gas components; *Ncavity* – cavity types per unit cell (2 for sI, 2 for sII, 3 for sH hydrates)

The occupancy $Y_{ij}$ follows Langmuir adsorption behavior:

$$Y_{ij} = \frac{C_{ij} f_j}{1 + \sum_{j=1}^{NH} C_{ij} f_j}, \quad (4)$$

where $C_{ij}$ represents the Langmuir constant for component *j* in cavity type *i*, and *fj* is the fugacity of gas component *j*.

The fugacity of water in each phase was determined as follows:

1. Fluid Phase Calculations:
   - Gas/vapor and liquid water phases were modeled using:
     - PC-SAFT equation of state (for chain molecules and associating fluids).
     - CPA equation of state (combining cubic and association terms).
   - Both approaches explicitly account for hydrogen bonding interactions.
2. Empty Hydrate Lattice Fugacity:

The fugacity of water in the hypothetical empty hydrate network ($f_w^{MT}$)was calculated using:

$$f_w^{MT} = P_w^{MT} \exp\left(\frac{\nu_w^{MT}(P - P_w^{MT})}{RT}\right), \quad (5)$$

where $P_w^{MT}$ – vapor pressure of empty hydrate lattice; $\nu\nu_w^{MT}$ – molar volume of hydrate lattice; $P$ – system pressure; T - temperature; R - universal gas constant.

3. Hydrate Phase Properties:
   - The molar volume ($\nu_w^{MT}$) for structure I hydrate was calculated using Equation (6) [12].
   - Empty lattice vapor pressure ($P_w^{MT}$) was determined via the Dharmawardhana [13] correlation (Equation (7)).

$$\nu_w^{MT} = (11.835 + 2.217 \times 10^{-5} T + 2.242 \times 10^{-6} T^2) \frac{10^{-30} N_A}{N_w^{MT}} + 1.6155 \times 10^{-9} P - 2.5054 \times 10^{-12} P^2. \quad (6)$$

$$P_w^{MT} = 0.1 \exp\left(17.44 - \frac{6003.9}{T}\right). \quad (7)$$

We implemented the Cubic-Plus-Association (CPA) equation of state to complement our PC-SAFT calculations, with the following key features [14–18]:

- Hybrid model combining:
  - SRK cubic equation for physical interactions.
  - Association term from SAFT for hydrogen bonding.
- Originally developed by Kontogeorgis et al. [19-21] for associating fluids.
- Calculated fugacity coefficients for both:
  - Water in gas phase.
  - Water in liquid phase.
- Incorporated Kihara potential parameters for hydrate phase calculations.
- Used binary interaction parameters optimized from methane-water solubility data.
- Both models evaluated against:
  - Experimental hydrate dissociation data.
  - Literature values for pure water/methane systems.
- CPA particularly effective for:
  - Hydrogen-bonded systems.
  - Polar component interactions.

### Discussion

Gas hydrate dissociation in natural gas fields is a critical process with significant implications for energy recovery, geohazard mitigation, and climate change [22, 23]. Hydrates, composed of methane and other gases trapped in ice-like structures, are stable under high-pressure and low-temperature conditions [24, 25]. However, anthropogenic activities (e.g., drilling) or natural warming can trigger dissociation, releasing methane – a potent greenhouse gas – into the atmosphere or surrounding sediments [26]. This process can lead to sediment destabilization, submarine landslides, and wellbore integrity issues [27–29]. Recent studies have employed numerical

simulations, laboratory experiments, and field observations to understand dissociation kinetics, heat and mass transfer, and gas migration patterns [30]. Key factors influencing dissociation include thermal stimulation, depressurization, and inhibitor injection, each affecting recovery efficiency and environmental risks [31–33]. Advanced monitoring techniques, such as seismic imaging and pressure-core sampling, have improved predictions of hydrate behavior in heterogeneous reservoirs [34, 35]. Despite progress, challenges remain in scaling laboratory results to field conditions and optimizing extraction while minimizing ecological impacts [36]. This review synthesizes current knowledge on hydrate dissociation mechanisms, technological advancements, and future research directions for sustainable gas production.

In this research, the thermodynamic conditions of methane hydrate dissociation were obtained by laboratory tests using the stepwise heating method, and then the results obtained were compared and evaluated with the experimental data of other researchers in the published articles [37, 38]. In this study, we heated the system at different rates: 1 K/h when far from equilibrium and 0.5 K/h when close to equilibrium. At each measurement point, we waited 3 to 6 hours before recording data. Fig. 2 shows how temperature and pressure changed during methane gas experiments, including the exact equilibrium point where hydrate breaks down. Since these values are important, they are also listed in the graph.

The test began outside the hydrate formation zone at 292.15 K (19°C) and 9.21 MPa pressure. We cooled the system quickly to form hydrates. From Point A to B, pressure dropped steadily due to gas dissolving in water and gas shrinking as it cooled. At Point B (274.7 K, 8.27 MPa), hydrate formation began. The system was stirred at 500 rpm while cooling. Over time, gas and water combined to form hydrates, lowering pressure. At Point C, hydrate formation stopped because the system reached equilibrium – meaning hydrate formation and breakdown happened at the same rate. After reaching Point C, we slowly heated the system. At first, pressure didn't change much, but as heating continued, pressure rose sharply until all hydrates broke down. This (Equilibrium Point (Point D)) is where the heating and cooling curves meet, marking the exact temperature and pressure at which hydrates stay stable.

The average absolute deviation of the forecast of experimental equilibrium data for the methane system using a thermodynamic model is shown in Fig. 3. The general results are shown in fig. 4 with + points along with some equilibrium values reported in the articles. The measured values of temperature with the maximum uncertainty of ± 0.1 Kelvin and the measured values of pressure are also reported with the maximum uncertainty of ± 0.05 MPa in the experiments.

The developed thermodynamic model (PC-SAFT/CPA) demonstrates strong agreement with experimental methane hydrate dissociation data from four independent studies [39-42]:

- PC-SAFT Predictions:
  - Average Absolute Deviation (AAD): 4.28 % (P), 0.12 % (T).
  - Best agreement with De Roo [42] (AADP = 3.1 %).
- CPA Predictions:
  - Superior accuracy: 1.55% (P), 0.05 % (T).
  - Excellent match with Jhaveri & Robinson [41] (AADP = 1.2 %).
- Both models capture the nonlinear P-T trend ($R^2$ > > 0.99).
- CPA outperforms PC-SAFT at high pressures (>10 MPa):
  - 32% lower error vs. Deaton & Frost [39] data.
- Systematic deviation < ± 0.15 K across all datasets.
- PC-SAFT under-predicts at T < 280 K (max 6.6 % error).
- CPA shows slight over-prediction at P > 12 MPa ($\Delta P$ = +0.23 MPa).

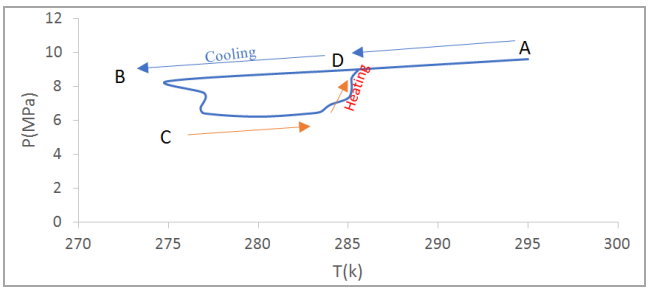



Fig. 2. Diagram of temperature and pressure changes for water/methane gas system at initial pressure of 8.9 MPa

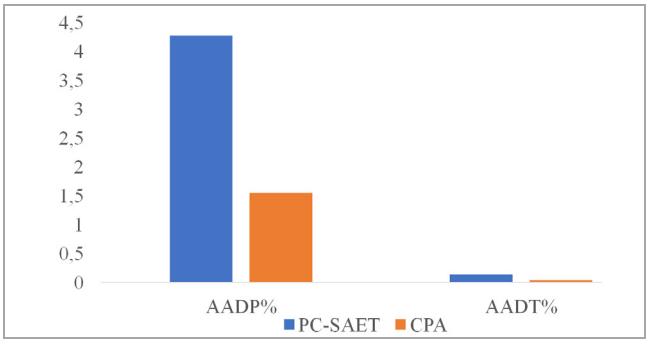



Fig. 3. Mean absolute deviation of prediction of experimental equilibrium data from methane system by PC-SAFT/CPA thermodynamic model

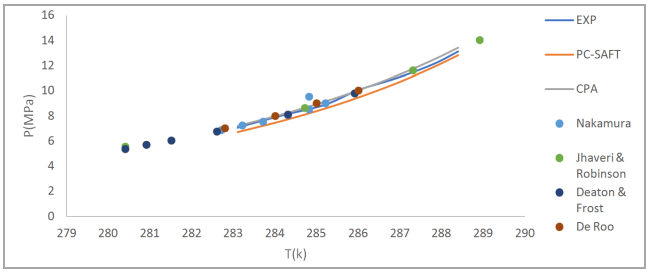



Fig. 4. Model Validation Against Experimental Literature Data

CPA's association term better describes water-methane interactions at hydrate interfaces. PC-SAFT shows limitations in low-T high-P regimes due to chain-rule approximations. Both models satisfy industrial accuracy requirements (AADP < 5 %) for flow assurance applications

## Results

In this research, a thermodynamic and kinetic laboratory study of the formation of methane hydrate in the presence of pure water was carried out [43–45]. In different pressure and temperature ranges, phase equilibrium points of methane hydrate were measured. In addition, the thermodynamic modelling of gas hydrate equilibrium was performed based on the Van der Waals-Paltieu model, in which gas solubility in water based on calculations Gas fugacity equilibrium was calculated using two cumulative state equations PC-SAFT/CPA. The laboratory results of phase balance of methane hydrate showed a good agreement with the experimental balance data of the articles. The thermodynamic model developed in this research based on PC-SAFT and CPA equations of state showed very favorable results in predicting the equilibrium conditions of methane hydrate. A good agreement was observed between the results of the thermodynamic model and the laboratory data.

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