



# Gas hydrate formation and dissociation numerical modelling with nitrogen and carbon dioxide



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## ABSTRACT

This work aims at providing experimental data for various methane-based hydrates, namely nitrogen and carbon dioxide gas mixtures with varying concentrations to provide an empirically based hydrate equilibrium model. Acquired using a sapphire pressure – volume – temperature (PVT) cell, this data is used as the foundation for the derivation of a model able to calculate the equilibrium temperature of a nitrogen and/or carbon dioxide diluted methane gas. There are several theoretical predictive models used in software which can provide hydrate formation and equilibrium data, however theoretical models appear to outnumber experimental data and empirical models for which a comparison can be made. The effect of nitrogen and carbon dioxide, a diluent and promotor respectively, on methane hydrate formation and dissociation and their associated pressure and temperature conditions are explored. The hydrate profiles for various gas mixtures containing these gases are presented at pressures ranging between 40 and 180 bara. These hydrate profiles and the model presented were compared to those predicted by hydrate computational software and experimental data from other studies for verification. The derived model proved to be reliable when applied to various gas mixtures at different pressure conditions and was consistent when compared to computational software based on theoretical models. Consistency of methane hydrate formation data was compared to dissociation data proved that the formation temperature is not an accurate representation of the equilibrium temperature. A simple statistical measure revealed the dissociation temperature measurements to be more precise and agreed to a much larger degree with literature.

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## 1. Introduction and background

Natural gas hydrates are crystalline solids composed of water and gas which occur in nature at high pressure and low temperature conditions (Sloan, 2008). The water (host) forms hydrogen bonded cavities which surround and enclathrate the gas (guest) molecule to form a crystalline solid resembling ice. Depending primarily on the size of the gas molecule, three different common gas hydrate structure types exist; structure I (sI), structure II (sII) and more recently structure H (sH). Smaller molecules such as methane, ethane and carbon dioxide typically form sI hydrates which are the most abundantly occurring hydrate structure in nature, with a preference to methane gas hydrates (Schicks, 2010).

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Natural gas hydrates continue to be a significant issue in oil and gas recovery and processing because of their ability to form in convenient operating conditions. High pressure and low temperature are ideal conditions for gas hydrate formation, however several other factors contribute to hydrate formation and their nature. In terms of stability, gas molecules are required to be small enough to fit inside the water cavities but also be large enough to provide stability to the hydrate structure (Buffet, 2000). A guest molecule approximately 75% the size of the cavity is required to provide adequate structural stability of the resultant hydrate whereas if the molecule is over 100% the size of the cavity, the structure cannot stabilize and the hydrate will not form (Christiansen and Sloan, 1994). A similar situation arises if the gas molecule size is significantly less than 75% of the cavity. In this case, the gas molecule is not large enough to supply adequate stability therefore preventing formation from occurring (Christiansen and Sloan, 1994). This has given rise to a significant amount of research in this field to combat the threats to productivity caused by gas hydrates.

Literature and experimental data informs us of nitrogen and carbon dioxide hydrate profiles but less of it is concerned with the effect these gases have on the hydrate profile of methane gas or natural gas for that matter, with methane being the primary component. Detailed in this article are hydrate profiles explaining and illustrating the effect these gases have on methane gas from a hydrate perspective via experimental data collected using a sapphire microcell. This study uses this information to construct an empirical model describing these equilibrium conditions. Additionally, this data is compared to computational software, namely Aspen HYSYS and Calsep PVTsim, to aid in the comparison between experimental and theoretical hydrate data and to confirm the reliability of the derived numerical model. The hydrate conditions predicted by these programs and their modes of calculation are investigated by inspecting the method, sources of necessary parameters such as critical properties and Langmuir constants associated with the equations of state (EOS) and hydrate equilibrium computations performed respectively. Each is compared to make a judgement on the cause of variation between predictions based on two equations of state, Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK). Experimental data from other works such as [Jhaveri and Robinson \(1965\)](#) and [Adisasmito et al. \(1991\)](#) are portrayed to illustrate the likeness to the model presented as well as any disagreement.

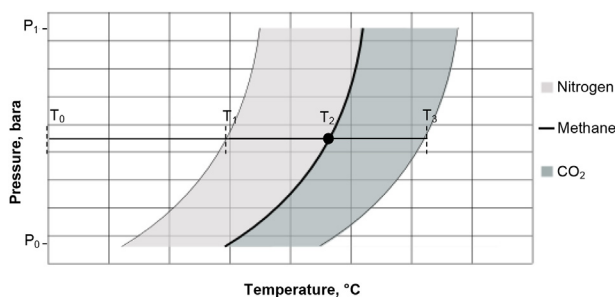
### 1.1. Empirical model derivation

Using experimental data, a relationship between the hydrate dissociation conditions of a methane-nitrogen-carbon dioxide gas can be developed. This can be achieved by deriving a constant based on how much the inclusion of nitrogen and carbon dioxide influence the dissociation temperature in a methane-based gas. The dissociation temperature of a gas mixture containing methane, nitrogen and/or carbon dioxide is empirically derived using the exponential equations that best describe the experimental nitrogen and carbon dioxide data.

The deviation from the methane reference due to nitrogen and carbon dioxide ([Fig. 1](#)) is summed by integrating between the appropriate pressure interval,  $P_1$ – $P_0$ . These are denoted  $\int_{P_0}^{P_1} (T_1 - T_0)dT$  for nitrogen and  $\int_{P_0}^{P_1} (T_3 - T_0)dT$  for carbon dioxide. These quantities are compared to pure methane,

$\int_{P_0}^{P_1} (T_2 - T_0)dT$ , in the form of a ratio,  $\frac{\int_{P_0}^{P_1} T_1 - T_0}{\int_{P_0}^{P_1} T_2 - T_0}$  for nitrogen and

$\frac{\int_{P_0}^{P_1} T_3 - T_0}{\int_{P_0}^{P_1} T_2 - T_0}$  for carbon dioxide. The dissociation temperature,  $T_d$ , is empirically expressed as,



**Fig. 1.** Methane hydrate profile shift.

$$T_d(P, x_{N_2}, x_{CO_2}) = T_2(P) + \ln(P/a_{N_2}) \frac{x_{N_2}}{x_{N_2,ref} b_{N_2}} \times \left( \frac{\int_{P_0}^{P_1} (T_1 - T_0)dT}{\int_{P_0}^{P_1} (T_2 - T_0)dT} - \frac{\int_{P_0}^{P_1} (T_2 - T_0)dT}{\int_{P_0}^{P_1} (T_2 - T_0)dT} \right) + \ln(P/a_{CO_2}) \frac{x_{CO_2}}{x_{CO_2,ref} b_{CO_2}} \times \left( \frac{\int_{P_0}^{P_1} (T_3 - T_0)dT}{\int_{P_0}^{P_1} (T_2 - T_0)dT} - \frac{\int_{P_0}^{P_1} (T_2 - T_0)dT}{\int_{P_0}^{P_1} (T_2 - T_0)dT} \right) \quad (1)$$

Symbols have their usual meaning; P and T are pressure and temperature respectively,  $x_{N_2}$  is the nitrogen mole fraction,  $x_{CO_2}$  is the carbon-dioxide mole fraction, a and b are constants from the exponential relation and  $x_{CO_2,ref}$  and  $x_{N_2,ref}$  are the mole fractions of the experimental gases used to generate data. Generating experimental hydrate profiles means the areas between the equilibrium lines can be evaluated. The model is not dependent on the volume of water present on the basis that the water volume is small and is insignificant compared to the moles of gas in each hydrate experiment. This is later shown to be valid ([Section 4.3.2](#)); the resultant model is presented in [Section 4.5](#).

## 2. Methodology

### 2.1. Introduction

The primary apparatus used for the research work was a sapphire cell and an associated flow loop housed at the Clean Gas Technologies Australia (CGTA) laboratory. CGTA specialises in hydrate technology and carbon dioxide capture. The simplistic flow loop was designed to be as accessible as possible predominantly because of the use of manual ball valves. All tubing used in the flow loop is 1/4 inch with all fittings.

The PVT cell ([Fig. 2](#)) is capable of enduring pressures in the vicinity of 500 bara and temperatures down to  $-160^\circ\text{C}$  when liquid nitrogen is used as the coolant, however cooling water is sufficient. For the purpose of this work, the PVT cell was operated in the ranges of 40–180 bara and 0–30 °C. The volume of the cell is 80 cm<sup>3</sup> non-inclusive of internal tubing; this cannot be ignored because the volume of gas in the tubing is 25.8 cm<sup>3</sup> based on its 74 cm length and 1/4 in diameter. This equates to a total volume of 105.8 cm<sup>3</sup>. The cell is protected by thick glass allowing it to experience high pressures and is separated from the outside environment by a reinforced and insulated door. Six clamps attached to the door allow for a tight seal, minimizing heat transfer through the housing of the PVT cell.

### 2.2. Application of apparatus

A piston pump is implemented for the pressurization of gas and is maintained via software that controls the position of the piston. Pressure is monitored by pressure sensors and controlled via a Baldor motion PID controller which is linked with Mint Workbench software for inputting pressure set points and monitoring. This

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