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# An Improved Description of Clathrate Hydrates Using Classical Density Functional Theory Coupled with a Simple Lattice Gas and Van der Waals-Platteeuw Theory

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## Abstract

The present study refines a recently published model which described clathrate hydrate phase equilibria by coupling the statistical mechanical van der Waals-Platteeuw approach with a mean-field lattice gas in the framework of classical density functional theory. This model yielded analytical expressions for the cavity occupancy, and requires, in principle, knowledge of only two parameters: The potential energy well depth, and a hard-sphere radius for the gas-water interaction. The present contribution expands on this model by examining the utility of several modifications in order to improve its accuracy in describing the dissociation pressure curves of a dozen clathrate hydrates: Argon, carbon dioxide, carbon monoxide, ethane, ethene, hydrogen sulphide, krypton, methane, nitrogen, propane, sulphur dioxide, and 1,1,1,2-tetrafluoroethane. A modified model is demonstrated which produced a good fit to experimental data for the 12 gas hydrate systems considered in this study, with an absolute average temperature deviation of less than 0.7 % in all cases.

*Keywords:* Clathrate hydrate, Thermodynamics, Phase equilibrium

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## 1. Introduction

### 1.1. Background

Clathrate hydrates, or gas hydrates, are an ice-like non-stoichiometric compound consisting of water and at least one volatile gas species. These hydrates can form blockages in offshore natural gas pipelines and may be problematic in the oil and gas industries [1]. Structurally, clathrate hydrates consist of crystals composed of cage-like cavities in which gas molecules may be found.

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