

## The Cage Specific Hydrate Equilibrium Electrolyte (CaSH-e) Model

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Understanding the thermophysical properties and phase behaviour of gas hydrates is essential for industrial applications ranging from energy transport and storage, CO<sub>2</sub> capture and sequestration, desalination, to gas production from hydrates found on the seabed. Current tools for predicting hydrate equilibrium boundaries typically use van der Waals-Platteeuw-type models, which are over-parameterised and contain terms with limited physical basis. Additionally, existing thermodynamic models that predict the influence of salts on hydrate dissociation temperatures often require numerous additional fitting parameters and are tailored to specific hydrate systems with limited generality.

Here we present a new model for hydrate equilibrium calculations with 40% fewer parameters than existing tools but with equivalent accuracy, including for multicomponent gas mixtures and/or systems with thermodynamic inhibitors. By eliminating multi-layered shells from the model's conceptual basis and focusing on Kihara potential parameters for guest-water interactions specific to each hydrate cavity type, this new model provides insight into the physical chemistry governing hydrate thermodynamics. The model retains the improved description of the empty lattice developed recently by Hielscher et al. (2018, *Fluid Phase Equilibria* 408, 38-46) but couples the hydrate model with a Cubic-Plus-Association Equation of State (CPA-EOS) to describe fluid mixtures with many more components including inhibitors such as methanol and mono-ethylene glycol used by industry.

This model has now been extended to include a physically-based description of the impact of electrolyte solutions on hydrate equilibria. Utilising an extended Debye-Hückel equation, we accurately describe osmotic coefficients for 191 unique single strong electrolyte solutions. Zdanovskii's rule is then employed to predict osmotic coefficients in mixtures of these electrolytes without the need for any additional fitting parameters.

The absolute average deviation in temperature (AADT) achieved with the new model is 0.92 K for uninhibited multicomponent gas mixtures, compared with 1.00 K for the widely-known model of Ballard and Sloan, and 0.86 K for the CPA-hydrates model implemented in the MultiFlash 7.0 (MF) package. These accurate predictions are maintained for multicomponent systems with MEG (AADT = 0.913 K vs MF = 0.899 K), salts (AADT = 1.26 K vs MF = 1.24 K), and mixtures of MEG and salts (AADT = 1.70 K vs MF = 1.55 K). With fewer, more physically justified parameters, this new cage-specific model provides a robust basis for improved hydrate equilibrium predictions particularly for industrially-important, multicomponent mixtures containing both thermodynamic inhibitors and salts.