

Supporting Information

A Cage-Specific Hydrate Equilibrium Model for Robust Predictions of Industrially-Relevant Mixtures

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1. Modelling details

1.1. Calculation of fugacity coefficients with CPA EOS

This section presents the equations required for the calculation of fluid phase fugacity coefficients with the CPA EOS. The methodology follows Michelsen and Mollerup¹ and Appendix 9C from Kontogeorgis and Folas², as the EOS is no longer cubic due to the association term present. From classical thermodynamics the fugacity coefficient φ_i of a component i in a mixture is given by:

$$RT \ln \varphi_i = \left(\frac{\partial A^r}{\partial n_i} \right)_{T,V,n_j} - RT \ln Z \quad (S1)$$

A^r is the residual Helmholtz energy of the mixture and Z is the compressibility factor:

$$Z = \frac{PV}{nRT} \quad (S2)$$

The CPA EOS combines the Soave-Redlich-Kwong EOS with the association term, derived from Wertheim's first-order perturbation theory. This means A^r has two contributions:

$$A^r(T, V, n) = A_{SRK}^r(T, V, n) + A_{association}^r(T, V, n) \quad (S3)$$

Michelsen and Mollerup¹ outline how the SRK term fugacity coefficient can be calculated:

$$\frac{A_{SRK}^r(T, V, n)}{RT} = -n \ln \left(1 - \frac{B}{V} \right) - \frac{D(T)}{RTB} \ln \left(1 + \frac{B}{V} \right) \quad (S4)$$

where V is the total volume of the system, while:

$$nB = n^2 b_{mix} = \sum_i n_i \sum_j n_j b_{ij} \quad (S5)$$

$$D(T) = n^2 a_{mix} = \sum_i n_i \sum_j a_{ij}(T) \quad (S6)$$

$$n = \sum_i n_i \quad (S7)$$

The classical van der Waals mixing rules are used for the energy term $\alpha(T)$ and co-volume parameter b :

$$a_{ij}(T) = a_{ji}(T) = \sqrt{a_{ii}(T)a_{jj}(T)}(1 - k_{ij}) \quad (\text{S8})$$

$$b_{ij} = b_{ji} = \frac{1}{2}(b_{ii} + b_{jj}) \quad (\text{S9})$$

Therefore, using Equation S9 reduces Equation S5 to:

$$B = \sum_i n_i b_{ii} \quad (\text{S10})$$

Assuming that:

$$\frac{A_{SRK}^r(T, V, n)}{RT} = -n \ln \left(1 - \frac{B}{V}\right) - \frac{D(T)}{RTB} \ln \left(1 + \frac{B}{V}\right) = F^{SRK} \quad (\text{S11})$$

$$g(V, B) = \ln \left(1 - \frac{B}{V}\right) \quad (\text{S12})$$

$$f(V, B) = \frac{1}{RB} \ln \left(1 + \frac{B}{V}\right) \quad (\text{S13})$$

By substituting Equations S12 and S13 into Equation S11, the resulting equation for F^{SRK} is given as:

$$F^{SRK} = -ng(V, B) - \frac{D(T)}{T} f(V, B) \quad (\text{S14})$$

Hence, calculation of the fugacity coefficient φ_i of a component i for the SRK term requires the derivative of the function F^{SRK} :

$$\left(\frac{\partial F^{SRK}}{\partial n_i}\right)_{T, V, n_j} = F_n + F_B B_i + F_D D_i \quad (\text{S15})$$

where:

$$F_n = -g = -\ln \left(1 - \frac{B}{V}\right) \quad (\text{S16})$$

$$F_b = -ng_B - \frac{D(T)}{T} f_B \quad (\text{S17})$$

with:

$$g_B = -\frac{1}{(V - B)} \quad (\text{S18})$$

$$f_B = -\frac{f + Vf_V}{B} \quad (\text{S19})$$

$$f_V = -\frac{1}{RV(V + B)} \quad (\text{S20})$$

$$F_D = -\frac{f}{T} \quad (\text{S21})$$

B_i and D_i are the composition derivatives of the energy term (Equation S6) and the co-volume term (Equation S10), and are given by the following equations:

$$B_i = \frac{2 \sum_j n_j b_{jj} - B}{n} \quad (\text{S22})$$

$$D_i = 2 \sum_j n_j a_{ij} \quad (\text{S23})$$

1.1.1. Association term of the CPA EOS

The approach proposed by Michelsen and Hendriks³ is used to estimate the contribution of the association term to the residual Helmholtz energy $A_{association}^r(T, V, n)$. They introduced a Q function for the calculation of the derived properties of the association term. This function takes advantage of the fact that the association contribution to the Helmholtz energy is itself the result of a minimisation:

$$Q(n, T, V, X) = \sum_i n_i \sum_{A_i} (\ln X_{A_i} - X_{A_i} + 1) - \frac{1}{2V} \sum_i \sum_j n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \partial^{A_i B_j} \quad (\text{S24})$$

In Equation S24, X_{A_i} is the fraction of A sites on molecule i that do not form bonds with other active sites, n is the total composition of the mixture and V is the total volume. The association conditions of the CPA EOS equals the value of Q at a stationary point with respect to the site fractions X . The stationary point representing these conditions is thus:

$$\frac{\partial Q}{\partial X_{A_i}} = 0, \quad \text{for all sites} \quad (\text{S25})$$

By differentiating Equation S24:

$$n_i \left(\frac{1}{X_{A_i}} - 1 \right) - \frac{1}{V} n_i \sum_j n_j \sum_{B_j} X_{B_j} \partial^{A_i B_j} = 0 \quad (\text{S26})$$

Which yields:

$$\frac{1}{X_{A_i}} = 1 + \frac{1}{V} \sum_j n_j \sum_{B_j} X_{B_j} \partial^{A_i B_j} \quad (\text{S27})$$

The value of Q at a stationary point (sp) is thus:

$$Q_{sp} = \sum_i n_i \sum_{A_i} (\ln X_{A_i} - X_{A_i} + 1) - \frac{1}{2} \sum_i n_i \sum_{A_i} X_{A_i} \left(\frac{1}{V} \sum_j n_j \sum_{B_j} \partial^{A_i B_j} \right) \quad (\text{S28})$$

$$\therefore Q_{sp} = \sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) = \frac{A_{association}^r(T, V, n)}{RT} \quad (\text{S29})$$

The chain rule is applied to calculate the fugacity coefficient from the association term. The derivative of Q_{sp} with respect to n_i is given by the following expression:

$$\frac{\partial Q_{sp}}{\partial n_i} = \frac{\partial Q}{\partial n_i} \Big|_X + \sum_i \sum_{A_i} \frac{\partial Q}{\partial X_{A_i}} \frac{\partial X_{A_i}}{\partial n_i} \quad (\text{S30})$$

However, at the stationary point, the derivatives $\partial Q / \partial X_{A_i}$ are by definition zero, meaning that the fugacity coefficient can now be calculated using the explicit derivative of Q with respect to n_i :

$$\begin{aligned} \frac{\partial}{\partial n_i} \left(\frac{A_{association}^r}{RT} \right)_{T,V,n_j} &= \frac{\partial}{\partial n_i} \left(\sum_i n_i \sum_{A_i} (\ln X_{A_i} - X_{A_i} + 1) - \frac{1}{2V} \sum_i \sum_j n_i n_j \sum_{A_i} \sum_{B_j} \Delta^{A_i B_j} \right)_{T,V,n_j} \\ &= \sum_{A_i} (\ln X_{A_i} - X_{A_i} + 1) - \frac{1}{2V} \frac{\partial}{\partial n_i} \Big|_{\Delta} \left(\sum_i \sum_j n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \Delta^{A_i B_j} \right) \\ &\quad - \frac{1}{2V} \sum_i \sum_j n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \frac{\partial \Delta^{A_i B_j}}{\partial n_i} \end{aligned} \quad (\text{S31})$$

When the yielding equation is combined with Equation S27 and after some algebra:

$$\begin{aligned}
& \frac{\partial}{\partial n_i} \left(\frac{A_{association}^r}{RT} \right)_{T,V,n_j} \\
&= \sum_{A_i} \ln X_{A_i} - \frac{1}{2V} \sum_i \sum_j n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \frac{\partial \Delta^{A_i B_j}}{\partial n_i}
\end{aligned} \quad (S32)$$

The derivative $\partial \Delta^{A_i B_j} / \partial n_i$ is given by the following equation:

$$\frac{\partial \Delta^{A_i B_j}}{\partial n_i} = \Delta^{A_i B_j} \frac{\partial \ln g}{\partial n_i} \quad (S33)$$

Combining Equation S32 with S33 gives:

$$\begin{aligned}
& \frac{\partial}{\partial n_i} \left(\frac{A_{association}^r}{RT} \right)_{T,V,n_j} \\
&= \sum_{A_i} \ln X_{A_i} - \frac{1}{2V} \sum_i \sum_j n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \Delta^{A_i B_j} \frac{\partial \ln g}{\partial n_i}
\end{aligned} \quad (S34)$$

Combining Equation S34 with S27 yields the final equation:

$$\frac{\partial}{\partial n_i} \left(\frac{A_{association}^r}{RT} \right) = \sum_{X_{A_i}} \ln X_{A_i} - \frac{1}{2} \sum_i n_i \sum_{A_i} (1 - X_{A_i}) \frac{\partial \ln g}{\partial n_i} \quad (S35)$$

Therefore, for the calculation of the contribution of the association term, the derivative of g with respect to n_i is required. Given that for the CPA EOS:

$$g(V, n) = \frac{1}{1 - 1.9\eta}, \quad \text{where} \quad \eta = \frac{B}{4V} \quad (S36)$$

and B is given by Equation S10, then:

$$\frac{\partial g}{\partial n_i} = \frac{\partial g}{\partial B} B_i \quad (S37)$$

where B_i can be calculated from Equation S22, while:

$$\frac{\partial g}{\partial B} = 0.475V \left(\frac{1}{V - 0.475B} \right)^2 \quad (S38)$$

1.2. Calculation of the Ideal Gas Gibbs Energy

The ideal gas Gibbs energy of pure water is calculated using the following expression, which is general to any component:

$$\frac{g_{w,o}}{RT} = \frac{g_{w_0,o}}{RT_0} - \int_{T_0}^T \frac{h_{w,o}}{RT^2} dT \quad (\text{S39})$$

Where $g_{w_0,o}$ is the molar Gibbs energy of formation at T_0 and P_0 . The enthalpy of the ideal gases is:

$$h_{w,o} = h_{w_0,o} + \int_{T_0}^T c_{P,w} dT \quad (\text{S40})$$

Where $h_{w_0,o}$ is the molar enthalpy of formation at T_0, P_0 , and $c_{P,w}$ is the heat capacity, which is of the form:

$$c_{P,w} = a_0 + a_1T + a_2T^2 + a_3^3 \quad (\text{S41})$$

Note that for the Gibbs energy and enthalpy of formation, a different reference state of $T_0 = 298.15$ K and $P_0 = 1$ bar is used. Table S1 below lists the constants used for calculating the water ideal gas Gibbs energy and the ideal gas heat capacity parameters.

Table S1: Ideal gas formation properties and heat capacity parameters for Equations S39, S40 and S41⁴.

Parameter	Value (Water)
$g_{w_0,o}$ (J/mol)	-228700
$h_{w_0,o}$ (J/mol)	-242000
a_0/R	3.8747
a_1/R	0.0231
a_2/R	0.1269
a_3/R	-0.4321

1.3. Calculation of the ice-phase fugacity

The equation used to calculate the fugacity of pure water in its solid (ice) phase, or for any pure component i in its solid phase, is given as:

$$\ln(f_{is}^S) = \ln(\varphi_{pure,i}^L P) - \frac{\Delta H_{f,i}}{RT_{m,i}} \left[\frac{T_{m,i}}{T} - 1 \right] + \frac{\Delta C_{p,i}^{L \rightarrow S}}{R} \left[\frac{T_{m,i}}{T} - 1 + \ln \left(\frac{T}{T_{m,i}} \right) \right] - \frac{\Delta v_i^{L \rightarrow S} (P - P_m)}{RT}$$

Where $\varphi_{pure,i}^L$ is the fugacity coefficient of pure component i in the liquid phase calculated with the CPA EOS; $T_{m,i}$ is the melting temperature of pure component i ; $\Delta H_{f,i}$ is the corresponding molar heat of fusion at $T_{m,i}$; $\Delta C_{p,i}^{L \rightarrow S}$ is the molar specific heat of the component as a pure liquid minus that of the pure solid i , which is approximated as independent of the temperature; $\Delta v_i^{L \rightarrow S}$ is the change in volume between the liquid and solid phase of component i ; and P_m is a reference pressure for the given melting temperature, which in this case is atmospheric pressure. (or any given pure component i)

2. Breakdown of number of tuneable parameters

This section gives a detailed breakdown of the number of tuneable parameters for each of the hydrate models considered in this work: the proposed cavity-based approach, Ballard and Sloan, and the Hielscher et al. model. The types of parameters can be broadly classified as either universal/(hydrate)-structure dependent, or component-specific i.e. dependent on the hydrate formers considered.

When comparing the hydrate-former dependent parameters between Ballard and Sloan and the cavity-based approach, we consider the following hydrate-forming components only from Ballard and Sloan:

1. Methane
2. Ethane
3. Propane
4. Isobutane
5. n-Butane
6. Carbon Dioxide
7. Nitrogen
8. Hydrogen Sulfide

For the Hielscher et al. model, since not all the aforementioned formers are available, the eight formers included in their model are considered:

1. Methane
2. Ethane
3. Propane
4. Argon
5. Oxygen
6. Carbon Monoxide
7. Carbon Dioxide
8. Nitrogen

2.1. Cavity-based model

The proposed cavity-based model has the following universal/structure-dependent parameters, as summarised in Table S2.

Table S2: Breakdown of the sources of universal model parameters and the final total for the proposed cavity-based hydrate model.

Description	Number of Parameters	Parameter symbols
Reference Gibbs Energy and Enthalpy of Empty Hydrate Lattice	$2 \times 2 = 4$ (2 per hydrate structure)	$g_{w,0}^\beta, h_{w,0}^\beta$
Thermal expansion of hydrate lattice	$3 \times 2 = 6$ (3 per hydrate structure)	$\alpha_1, \alpha_2, \alpha_3$
Reference lattice parameters	2	$a_{0,ref}$
Compressibility of hydrate lattice	2	B_0, B_0'
Cavity radii and coordination numbers	$2 \times 3 = 6$ (2 parameters for 3 cavity types)	R_i, z_i
Total	20	-

The component-specific parameters in this model are solely the Kihara Potential Parameters (KPP) $a_{c,i,J}$, $\sigma_{i,J}$, and $\frac{\epsilon_{i,J}}{k_B}$, for each hydrate former J and cavity type i . Since we consider three cavity types 5^{12} , $5^{12}6^2$ and $5^{12}6^4$, for n hydrate formers considered, we have a conservative estimate of $9n + 20$ parameters. When we consider $n = 8$ hydrate formers, this leads to a

conservative total of 92 parameters. However, in practice, there will often be components where only one set of cavity-specific parameters are required; for example, propane only occupies the large $5^{12}6^4$ sII large cavity and thus only has three KPP instead of the full nine per former. Additionally, in this implementation, we keep the hard core radius $a_{c,i,J}$ consistent between each of the cavity-specific parameter sets, which reduces the a_c values needed per hydrate former from three to one. Therefore, this model has a more realistic estimate of $7n + 20$ parameters; for 8 hydrate formers considered, this would total 76 parameters.

A precise count of the number of Kihara potential parameters required based on the tuned parameters in Table 12 of the main article yields a total of 44 parameters. Combined with the 20 universal/structure-based parameters, the total number of tuneable parameters for the cavity-based model is 64.

2.2. Ballard and Sloan parameter breakdown

Table S3 shows the breakdown of universal/structure-dependent parameters for the Ballard and Sloan hydrate model. A large number of these parameters come from the multi-layered shell approach used by BALLARD AND SLOAN: the values used in their work are shown in Table S4.

Table S3: Breakdown of the sources of universal model parameters and the final total for the Ballard and Sloan model.

Description	Number of Parameters	Parameter symbols
Reference Gibbs Energy and Enthalpy of Empty Hydrate Lattice	$4 \times 2 = 8$ (2 per hydrate structure)	$g_{w,0}^\beta, h_{w,0}^\beta, a, b$
Thermal expansion of hydrate lattice	$3 \times 2 = 6$ (3 per hydrate structure)	$\alpha_1, \alpha_2, \alpha_3$
Cavity radii and coordination numbers	24 for multilayered shell (Table S4)	R_i, z_i
Total	38	-

Table S4: Coordination numbers z_i and shell radii R_i assuming the guest molecule interacts with the first water shell, which is subdivided into four possible layers⁵

Cavity	First Layer		Second Layer		Third Layer		Fourth Layer	
	$R_{i,1} / \text{\AA}$	z_1	$R_{i,2} / \text{\AA}$	z_2	$R_{i,3} / \text{\AA}$	z_3	$R_{i,4} / \text{\AA}$	z_4
sI, small	3.83	8	3.96	12				
sI, large	4.06	8	4.25	4	4.47	8	4.645	4
sII, small	3.748	2	3.845	6	3.956	12		
sII, large	4.635	12	4.715	12	4.729	4		

The source of the additional a and b parameters come from the additional activity coefficient of the hydrate that Ballard and Sloan use to describe the chemical potential of water in the hydrate phase, which is described in their work as:

$$\mu_w^H = g_w^\beta + RT \sum_i v_i \ln \left(1 - \sum_J \theta_{i,J} \right) + \ln \gamma_w^H \quad (\text{S42})$$

where

$$\ln \gamma_w^H = \frac{\Delta g_{w,0}^\beta}{RT_0} + \frac{\Delta h_{w,0}^\beta}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \int_{P_0}^P \frac{\Delta v_H}{RT} dP \quad (\text{S43})$$

The terms $\frac{\Delta g_{w,0}^\beta}{RT_0}$ and $\frac{\Delta h_{w,0}^\beta}{R}$ represent the perturbed Gibbs energy and enthalpy of formation from the change of hydrate volume from the standard state lattices that Ballard and Sloan proposed to the volume of the real hydrate. These were assumed to be linear in this change of volume Δv_{H_0} :

$$\Delta g_{w,0}^\beta = a \Delta v_{H_0} \quad \text{and} \quad \Delta h_{w,0}^\beta = b \Delta v_{H_0} \quad (\text{S44})$$

These parameters a and b are structure-specific, resulting in a total of $2 \times 2 = 4$ parameters.

2.2.1. Component-specific parameters

The component-specific parameters involved in the Ballard and Sloan are more involved and are summarised in Table S5.

Table S5: Breakdown of hydrate-former dependent parameters' source and number for the Ballard and Sloan model. The total number of parameters is considered for $n = 8$ hydrate formers

Description	Number of Parameters	Parameter symbols
Kihara Potential Parameters	$3n = 24$	$a_c, \sigma, \frac{\epsilon}{k_B}$
Compressibility of hydrate lattice	Max of $2n \rightarrow 14$ for 8 formers in B&S	κ
Repulsive constants for Cavity radius/coordination numbers	Max of $4n \rightarrow 19$ for 8 formers in B&S	$\Delta r_{i,J}$
Guest molecular diameter	$n = 8$	D_J
Total	65	-

While Ballard and Sloan only use one set of Kihara potential parameters across all cavities and structures, the complexity comes from their description of hydrate volume compressibility, which is former-specific, and the use of repulsive constants in calculating the volume of the standard hydrate v_0 at T_0 and P_0 :

$$v_0(\bar{x}) = \left(a_0 * + \sum_i N_i \sum_i f(\theta_{i,J}) \Delta r_{i,J} \right) \quad (\text{S45})$$

where $\Delta r_{i,J}$ is the aforementioned repulsive constant for guest molecule J in hydrate cavity type i . Each hydrate former can have up to four possible Δr parameters: for the sI small, sI large, sII small, and sII large cavities that Ballard and Sloan consider, though in practice, no hydrate former has more than three non-zero Δr parameters⁴. The function $f(\theta_{i,J})$ is defined for the 5¹² hydrate cage as:

$$f(\theta_{i,J}) = \frac{(1 + \eta_i)\theta_{i,J}}{1 + \eta_i\theta_{i,J}} \exp[D_J - \bar{D}] \quad (\text{S46})$$

where D_J is the molecular diameter of component J , \bar{D} is the fractional occupancy average molecular diameter of the guest molecules in the hydrate, and η_i is the coordination number of cavity i (z_i) per water molecule in the hydrate N_w . Here, D_J incurs an additional set of parameters per hydrate former considered.

The compressibility parameter κ is used in the expression for the hydrate volume of Ballard and Sloan, which is structure-dependent:

$$v_H = v_0 \exp[\alpha_1(T - T_0) + \alpha_2(T - T_0)^2 + \alpha_3(T - T_0)^3 - \kappa(P - P_0)] \quad (\text{S47})$$

Thus, hydrate formers that can form both sI and sII hydrates (methane, ethane, CO₂) will have two parameters covering these structures, while formers such as propane, n-butane, i-butane will have one. Thus, the maximum number of parameters associated is $2n$ for n hydrate formers, while the actual parameter count will vary with the hydrate formers considered.

2.3. Hielscher parameter breakdown

Table S6 summarises the universal/structure-dependent parameters for the Hielscher model. As the cavity-based approach uses the Hielscher model as a base, it shares many similarities in the universal parameters for the empty hydrate lattice. The key difference from Table S2 is the removal of the multilayered shell description and the simplification of the reference lattice parameters to be independent of the hydrate former.

Table S6: Breakdown of the number universal parameters and their source in the Hielscher et al. hydrate model.

Description	Number of Parameters	Parameter symbols
Reference Gibbs Energy and Enthalpy of Empty Hydrate Lattice	$2 \times 2 = 4$ (2 per hydrate structure)	$g_{w,0}^{\beta}, h_{w,0}^{\beta}$
Thermal expansion of hydrate lattice	$3 \times 2 = 6$ (3 per hydrate structure)	$\alpha_1, \alpha_2, \alpha_3$
Compressibility of hydrate lattice	2	B_0, B_0'
Cavity radii and coordination numbers	24 for multilayered shell (Table S4)	R_i, z_i
Total	36	-

2.3.1. Hydrate former specific parameters

Table S7 summarises the parameters that are dependent of the hydrate formers considered for the Hielscher model.

Table S7: Breakdown of the number of hydrate former specific parameters and their source in the Hielscher et al. model. The total number of parameters is considered for $n = 8$ hydrate formers. It must be noted that the Hielscher et al. model also considers double occupancy of

hydrates, which adds a significant number of parameters; for fairness, these are excluded in the comparisons in the main paper.

Description	Number of Parameters	Parameter symbols
Kihara Potential Parameters	$2 \times 3n = 6n \rightarrow$ excluding a_c repeat: $5n = 40$	$a_c, \sigma, \frac{\epsilon}{k_B}$
Reference Lattice Parameters	$2 \times n = 2n = 16$ (n per hydrate structure)	$a_{0,J}^\beta$
Double occupancy parameters	$2 \times 3n = 6n = 48$ per hydrate structure	$r_{vdw,J}, \sigma_J^{gg}, \frac{\epsilon_J^{gg}}{k_B}$
Total without double occupancy	56	-
Total with double occupancy	104	-

The KPP sets are taken directly from Hielscher's thesis⁶, which lists two independent sets of KPPs specific to sI and sII hydrates. Given that a_c is kept constant between the two structures, for parameters $\sigma_{i,J}$ and $\left(\frac{\epsilon}{k_B}\right)_{i,J}$ for structure type i and hydrate former J yields a total of $5n$ parameters for n hydrate formers considered. When considering $n = 8$ hydrate formers, this leads to a total of 40 parameters.

2.3.2. Double occupancy modelling

The extension of the Hielscher model to capture double occupancy of hydrate cavities in Hielscher et al.⁷ adds a significant amount of component-specific tuneable parameters. Each hydrate former J has additional parameters $r_{vdw,J}, \sigma_J^{gg}$ and ϵ_J^{gg} to account for the double-occupancy contribution towards the fractional occupancy of the hydrate former, $\theta_{i,J}$. Furthermore, these parameters are structure-specific as well, which results in an additional total of $2 \times 3n = 6n$ parameters for n hydrate formers considered. For $n = 8$ hydrate formers, this leads to an additional 48 parameters associated with double occupancy modelling.

3. Hydrate Equilibrium Database Tables

This section shows the breakdown of datasets use for training the new cavity-based hydrate model and evaluating the model's performance against unseen data. It also includes the absolute average deviation of temperature (AADT) for each data set considered, including the predictions from both CPA-Hydrates as implemented in MultiFlash 7.0 (CPAHYD-MF), and Ballard and Sloan (B&S), as implemented in CSMGem 2007 (v1.1). Table S8 summarises the basic nomenclature used for the 'Phases' column of the following database tables.

Table S8: Nomenclature of phase types used in Database Tables

Phase types	Description
Lw	Liquid water phase
H	Hydrate phase
V	Vapour phase
I	Ice phase
LHC	Liquid hydrocarbon phase

Accompanying these datasets are figures showcasing the hydrate equilibrium data from most of the datasets (but not all of them). For visual clarity, only the model predictions from this work and MultiFlash will be plotted on these figures alongside the experimental data as black and red solid lines, respectively. Where applicable, distinct phases within a given dataset will be represented with different linetypes e.g. solid, dashed, dotted etc.

3.1. Simple Hydrate Equilibria

3.1.1. CH₄ simple hydrate equilibria

Table S9: Database of CH₄ simple hydrate equilibrium data, with comparison of the AADT of the cavity-based model against CPAHYD-MF and B&S. Data Types: "Tr" = Training Data; "Te" = Test Data.

Reference	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N	Type
Adisasmito et al. (1991) ⁸	Lw-H-V	0.106	0.105	0.109	273.4	286.4	2.68	10.57	11	Tr
Aghajanloo et al. (2020) ⁹	Lw-H-V	0.098	0.106	0.075	283.1	288.4	7.13	13.16	7	Tr
Blanc and Tournier-Lasserre (1990) ¹⁰	Lw-H-V	0.235	0.225	0.259	279.65	305.15	5	92	12	Te
Bottger et al. (2016) ¹¹	Lw-H-V	0.117	0.055	0.125	274.19	285.14	2.945	8.895	13	Te
Chen et al. (2009) ¹²	Lw-H-V	0.201	0.158	0.167	276.95	286.85	3.88	11.08	6	Te
Clarke and Bishnoi (2001) ¹³	Lw-H-V	1.023	0.945	1.042	274.65	281.15	3.187	7.487	21	Te
de Menezes et al. (2020) ¹⁴	Lw-H-V	0.393	0.786	0.324	281.01	305.26	5.5	100	11	Tr
de Roo et al. (1983) ¹⁵	Lw-H-V	0.212	0.184	0.186	273.3	286	2.69	10.04	9	Te
Deaton and Frost (1946) ¹⁶	Lw-H-V	0.066	0.132	0.060	273.7	285.9	2.77	9.78	13	Te
Deng et al. (1993) ¹⁷	Lw-H-V	0.256	0.279	0.201	274.9	284.85	3	9	5	Te
Dickens et al. (1994) ¹⁸	Lw-H-V	0.154	0.186	0.154	276.1	285.4	3.45	9.58	7	Te
Dyadin and Aladko (1996) ¹⁹	Lw-H-V	0.609	0.817	0.590	287	308.6	8	133	6	Te
Galloway et al. (1970) ²⁰	Lw-H-V	0.188	0.193	0.272	283.2	288.7	7.1	13.11	4	Te
Gayet et al. (2005) ²¹	Lw-H-V	0.116	0.151	0.076	275.15	300.15	3.17	54.53	26	Tr
Guo et al. (1992) ²²	Lw-H-V	0.106	0.105	0.109	273.4	286.4	2.68	10.57	11	Te
Hachikubo et al. (2002) ²³	Lw-H-V	1.148	0.863	1.721	268.4	271.28	2.324	2.527	2	Te
Hu et al. (2017a) ²⁴	Lw-H-V	0.317	0.662	0.178	295.75	309.85	34.3	150.1	5	Te
Hu et al. (2017b) ²⁵	Lw-H-V	0.317	0.662	0.178	295.75	309.85	34.3	150.13	5	Te
Hutz and Englezos (1996) ²⁶	Lw-H-V	0.215	0.199	0.190	274.6	285.35	3.021	9.35	7	Te
Jager (2001) ²⁷	Lw-H-V	0.398	0.581	0.363	278.1	302.1	4.05	72.85	11	Tr
Jager and Sloan (2001) ²⁸	Lw-H-V	0.312	0.371	0.309	291.86	303.48	20.19	72.26	12	Tr
Javanmardi et al. (2012) ²⁹	Lw-H-V	0.159	0.240	0.155	274.7	282	3.05	6.29	7	Te
Jhaveri and Robinson (1965) ³⁰	Lw-H-V	0.211	0.232	0.162	273.2	294.3	2.65	28.57	8	Te
Kamari et al. (2017) ³¹	Lw-H-V	0.040	0.063	0.060	274.3	285.8	2.92	9.54	17	Tr
Kharrat and Dalmazzone (2003) ³²	Lw-H-V	0.246	0.282	0.294	281.2	284	5.73	7.68	3	Te
Kobayashi and Katz (1949) ³³	Lw-H-V	0.347	0.532	0.271	295.7	295.9	33.99	35.3	2	Te
Komai et al. (1997) ³⁴	Lw-H-V	0.332	0.369	0.323	278.15	291.15	4.2	18.6	8	Te

Reference	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N	Type
Lafond et al. (2012) ³⁵	Lw-H-V	0.050	0.074	0.084	279.72	285.2	5	9	5	Te
Lim et al. (2017) ³⁶	Lw-H-V	0.190	0.203	0.244	281.5	291.6	5.7	19.61	6	Te
Maekawa (2001) ³⁷	Lw-H-V	0.107	0.114	0.145	274.2	288.2	2.9	12.6	30	Tr
Maekawa (2008a) Pure Water Lw-H-V ³⁸	Lw-H-V	0.107	0.163	0.125	274.6	286.9	3	10.8	9	Tr
Marshall et al. 1964a ³⁹	Lw-H-V	0.133	0.218	0.183	290.2	306.7	15.9	110.8	11	Tr
McLeod and Campbell (1961) ⁴⁰	Lw-H-V	0.174	0.300	0.115	285.7	301.6	9.62	68.09	9	Te
Mohammadi et al. (2003) ⁴¹	Lw-H-V	0.243	0.175	0.251	278.85	278.85	4.72976	4.72976	1	Te
Mohammadi et al. (2005) ⁴²	Lw-H-V	0.179	0.246	0.138	274.6	298.3	3.06	47.863	11	Te
Mu et al. (2018) ⁴³	Lw-H-V	0.170	0.212	0.166	275.54	286.35	3.163	10.143	10	Tr
Nakamura et al. (2003) ⁴⁴	Lw-H-V	0.012	0.066	0.054	274.25	285.78	2.92	9.54	17	Te
Nakano et al. (1999) ⁴⁵	Lw-H-V	0.372	0.773	0.205	305.08	308.74	98	138	3	Te
Nixdorf and Oellrich (1997) ⁴⁶	Lw-H-V	0.051	0.090	0.052	273.49	293.57	2.716	24.959	30	Tr
Ohgaki et al. (1996) ⁴⁷	Lw-H-V	0.205	0.151	0.192	280.3	280.3	5.46	5.46	1	Te
Ohmura et al. (2002) ⁴⁸	Lw-H-V	1.639	1.542	1.690	275	275	3.7	3.7	1	Te
Pahlavanzadeh et al. (2020) ⁴⁹	Lw-H-V	0.126	0.146	0.117	275.3	279.26	3.2	4.74	5	Tr
Roberts et al. (1940) ⁵⁰	Lw-H-V	0.200	0.184	0.123	280.9	286.7	5.847	10.8	3	Te
Saberi et al. (2018) ⁵¹	Lw-H-V	0.249	0.215	0.236	279	282.1	4.73	6.73	6	Te
Sabil et al. (2014) ⁵²	Lw-H-V	0.671	0.662	0.590	280.15	288.65	5.55	15.29	9	Te
Sadeq et al. (2017) ⁵³	Lw-H-V	0.464	0.489	0.383	279.45	292.95	5	25	6	Te
Sami et al. (2013) ⁵⁴	Lw-H-V	0.405	0.363	0.368	279.9	283.56	5.25	7.98	4	Te
Servio and Englezos (2002) ⁵⁵	Lw-H-V	0.106	0.291	0.072	276.25	282.05	3.5	6.5	3	Te
Smelik and King (1997) ⁵⁶	Lw-H-V	0.325	0.416	0.222	273	284.5	2.482	8.356	6	Te
Sun et al. (2018) ⁵⁷	Lw-H-V	0.071	0.070	0.042	280.9	289	5.7	14	9	Tr
Svartas and Fadnes (1992) ⁵⁸	Lw-H-V	0.216	0.334	0.189	271.8	297.1	2.41	39.31	12	Te
Svartas and Fadnes (1992) 0.57 wt% MeOH Lw-H-V ⁵⁸	Lw-H-V	0.055	0.197	0.109	299.2	299.2	49.96	49.96	1	Te
Thakore and Holder (1987) ⁵⁹	Lw-H-V	0.484	0.435	0.469	274.35	281.2	2.87	6.1	7	Te
Verma (1974) ⁶⁰	Lw-H-V	0.176	0.219	0.190	275.2	291.2	3.02	18.55	7	Te
Ward et al. (2015) ⁶¹	Lw-H-V	0.067	0.075	0.042	276.29	285.57	3.53	9.38	8	Tr
Xiao et al. (2019) ⁶²	I-H-V	0.528	0.160	1.159	263.15	268.15	1.93	2.24	2	Tr
	Lw-H-V	0.653	0.586	0.719	273.15	303.15	2.64	65.81	7	Tr
Xu et al. (2017) ⁶³	Lw-H-V	0.094	0.122	0.119	285.65	291.65	9.5	20.1	4	Te
Yang et al. (2001) ⁶⁴	Lw-H-V	0.185	0.180	0.200	276.5	286.3	3.68	9.66	10	Tr
Yasuda and Ohmura (2008) ⁶⁵	I-H-V	0.512	0.717	0.388	244.2	272.9	0.971	2.543	17	Tr

Reference	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N	Type
	Lw-H-V	0.190	0.355	0.074	272.9	274.7	2.53	3.016	13	Tr
Training	—	0.185	0.248	0.175	244.2	306.7	0.971	110.8	256	—
Test	—	0.298	0.335	0.286	268.4	309.85	2.324	150.13	276	—
Overall	—	0.244	0.293	0.233	244.2	309.85	0.971	150.13	532	—

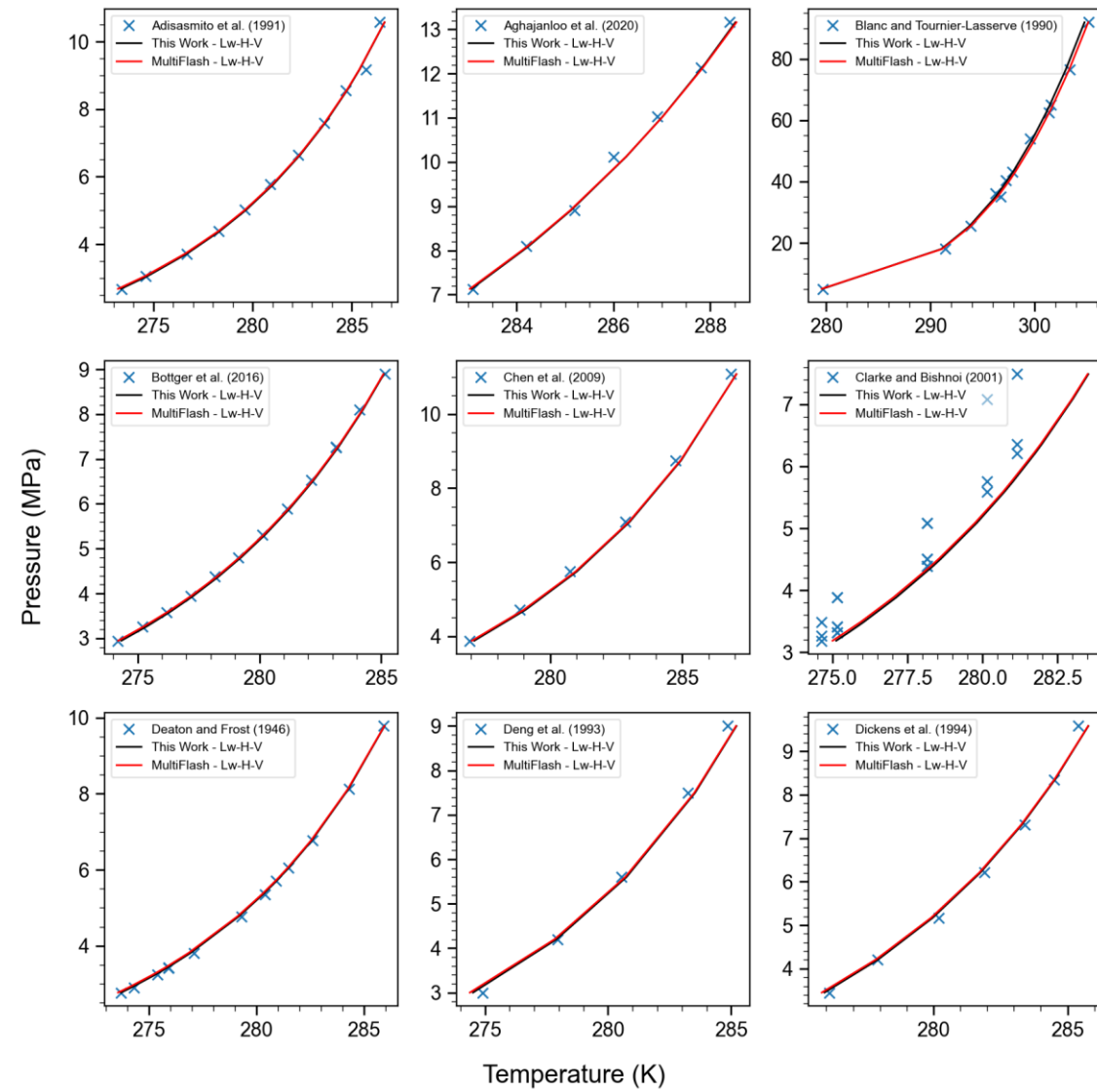


Figure S1: Selected hydrate equilibrium datasets (group 1) for simple CH_4 hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{8-13,16-18}

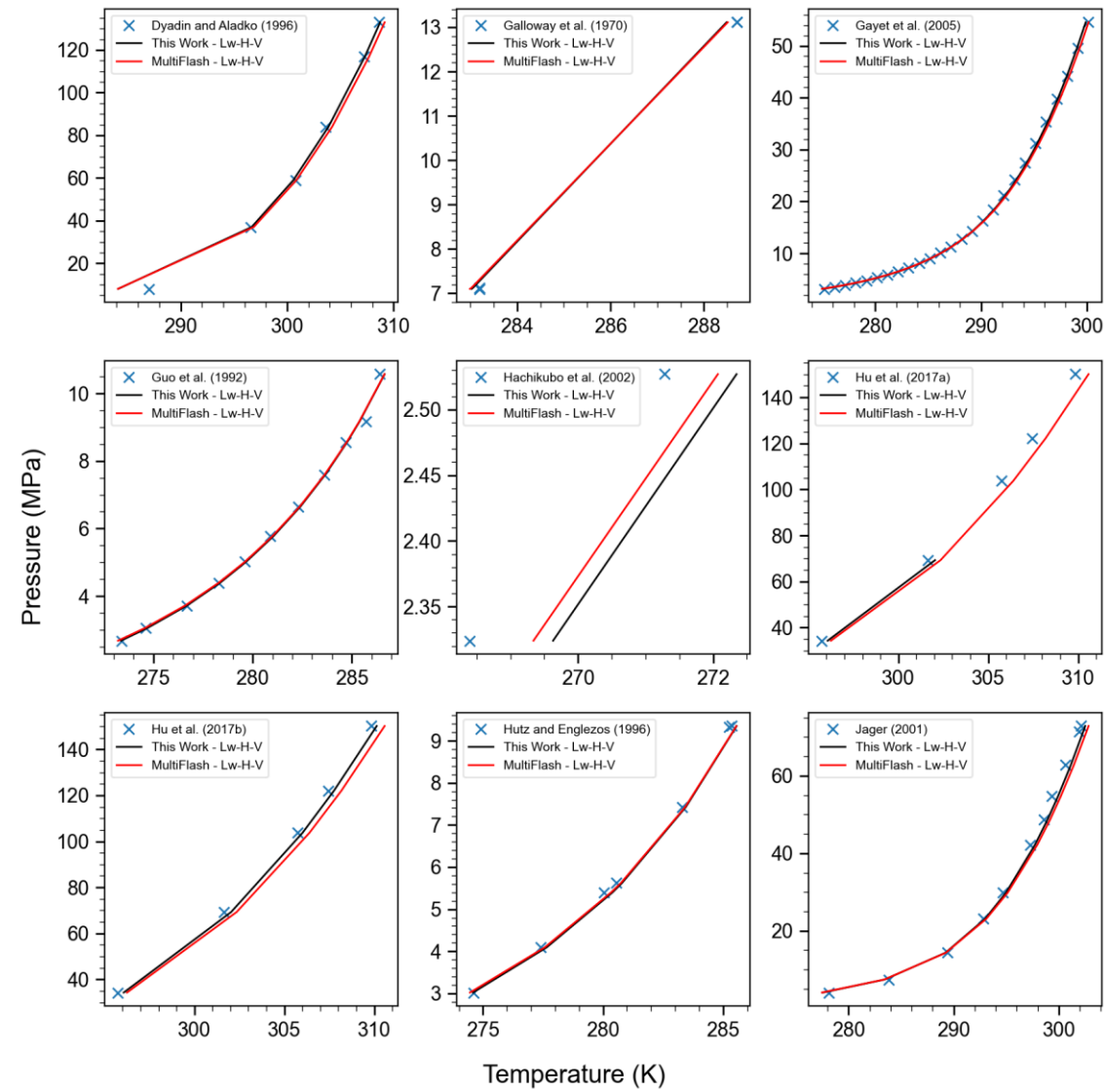


Figure S2: Selected hydrate equilibrium datasets (group 2) for simple CH_4 hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:¹⁹⁻²⁷

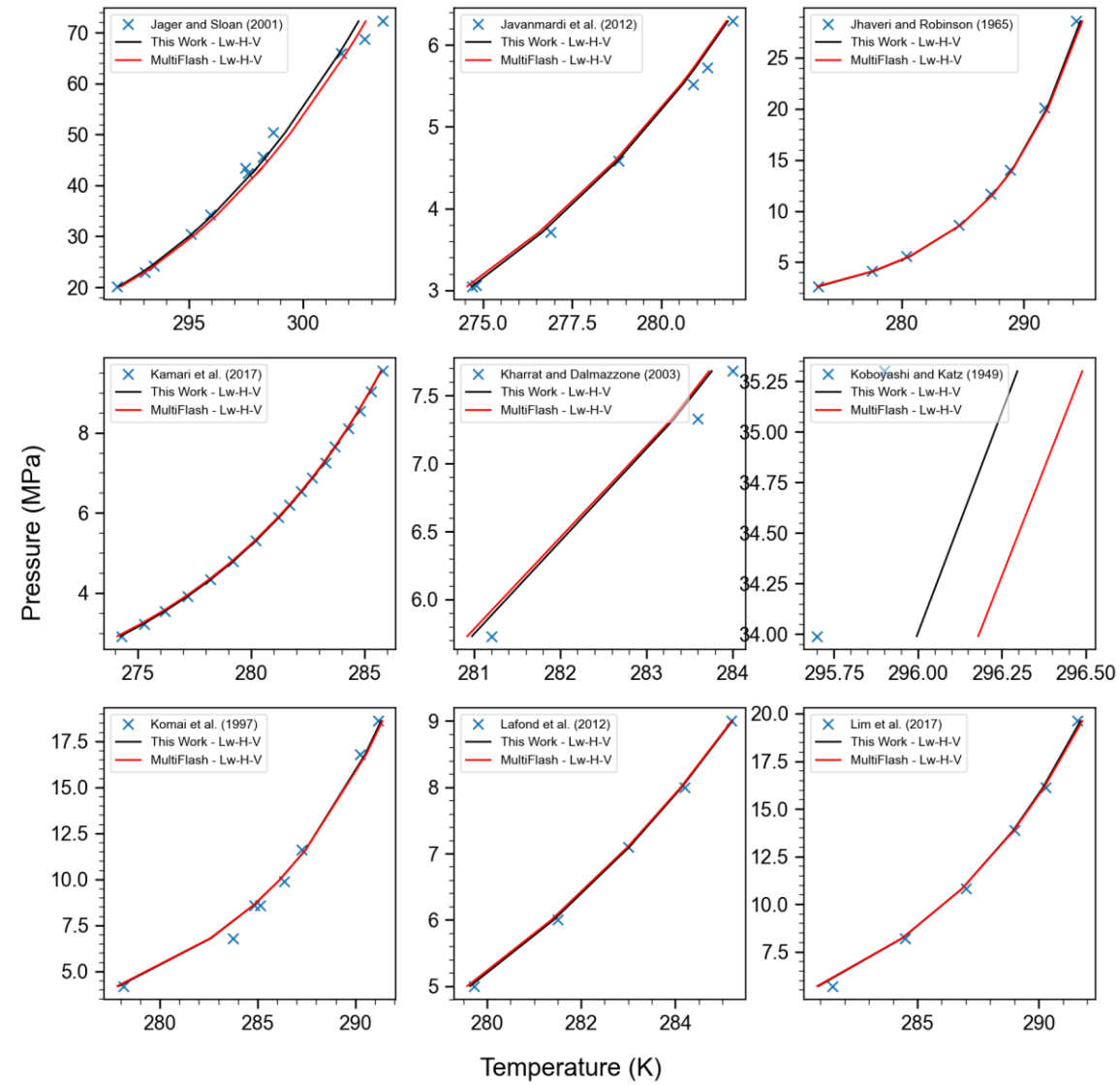


Figure S3: Selected hydrate equilibrium datasets (group 3) for simple CH_4 hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:²⁸⁻³⁶

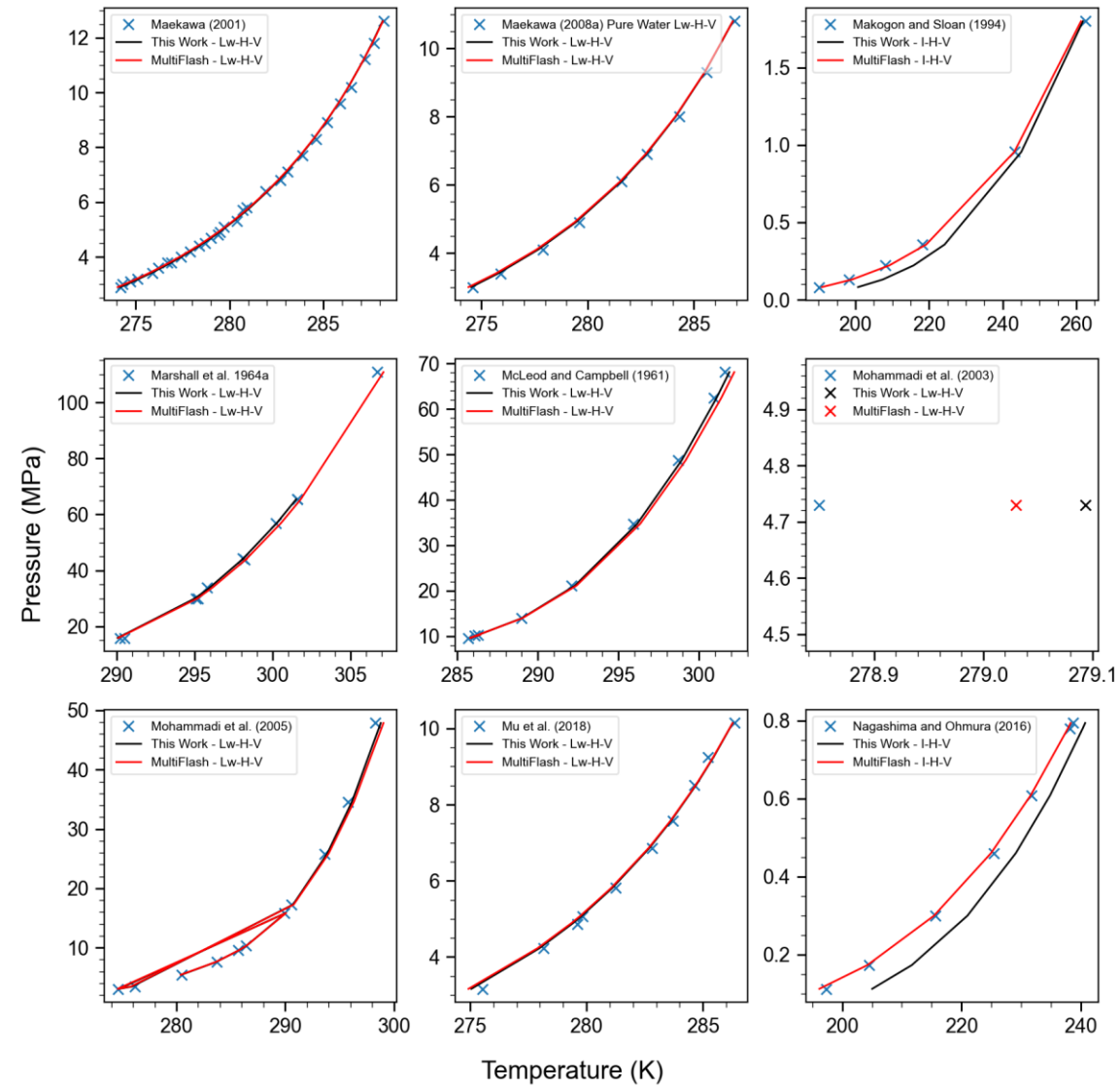


Figure S4: Selected hydrate equilibrium datasets (group 4) for simple CH₄ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{37-43,66,67}

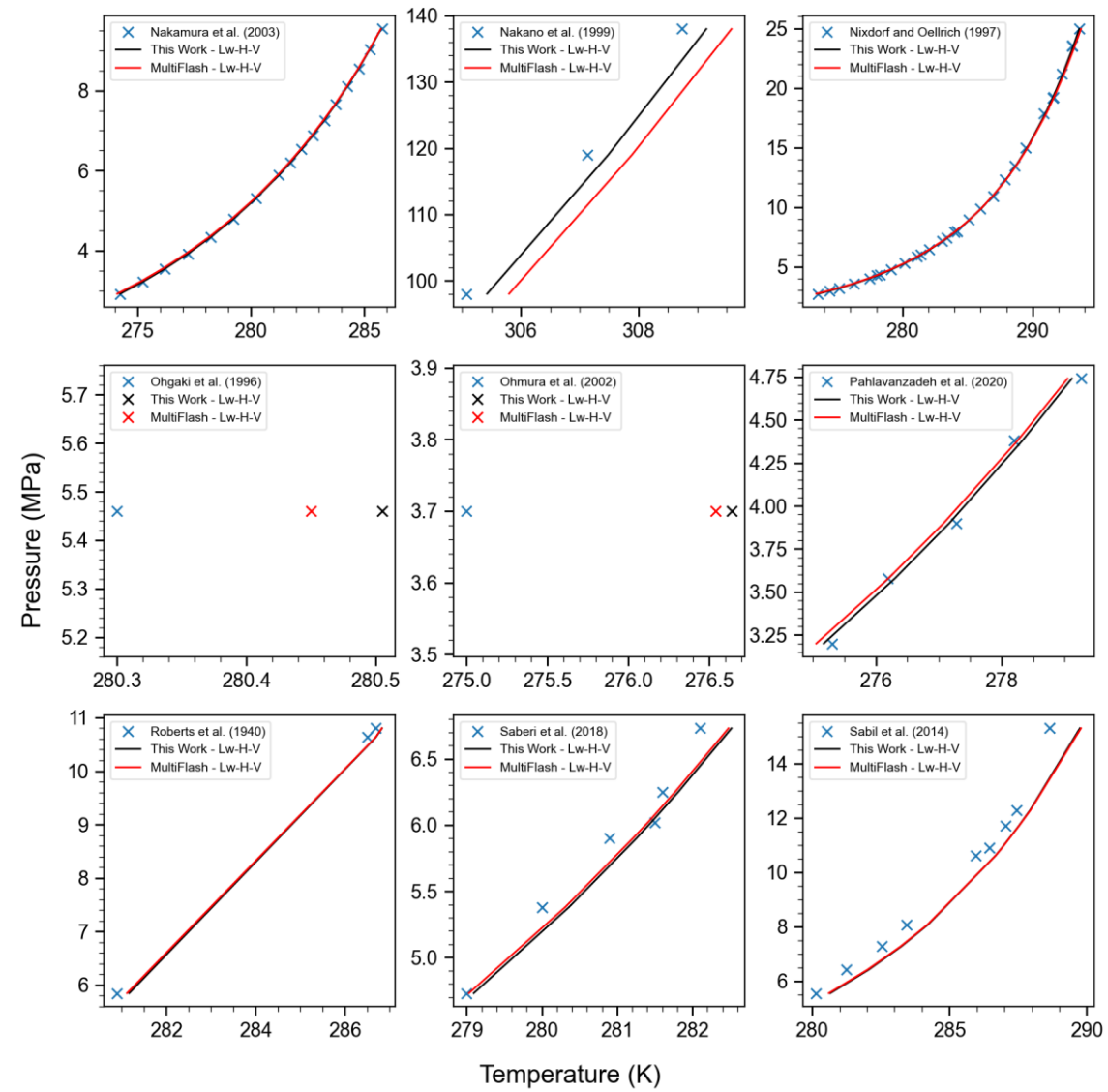


Figure S5: Selected hydrate equilibrium datasets (group 5) for simple CH₄ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:⁴⁴⁻⁵²

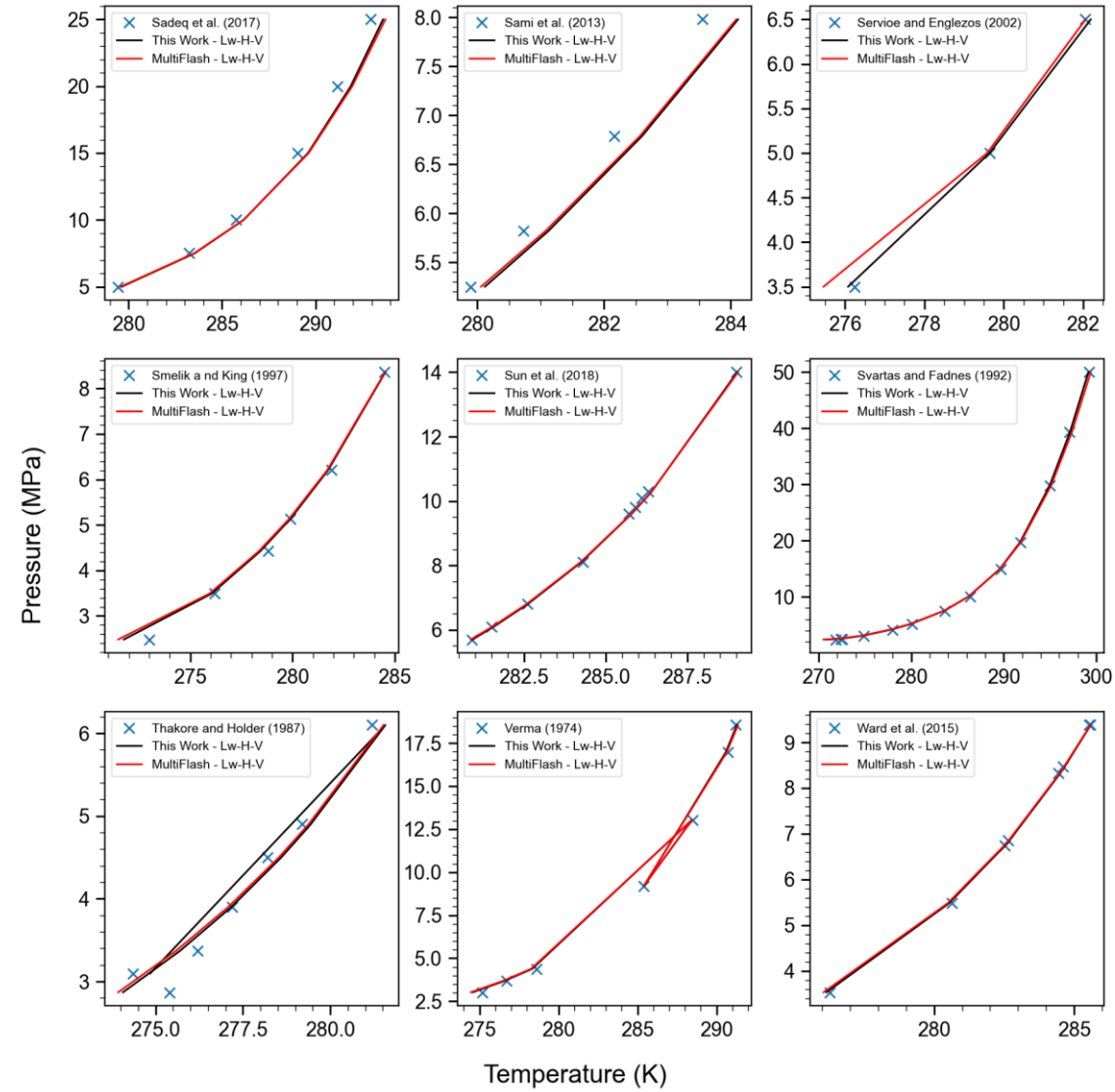


Figure S6: Selected hydrate equilibrium datasets (group 6) for simple CH_4 hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:⁵³⁻⁶¹

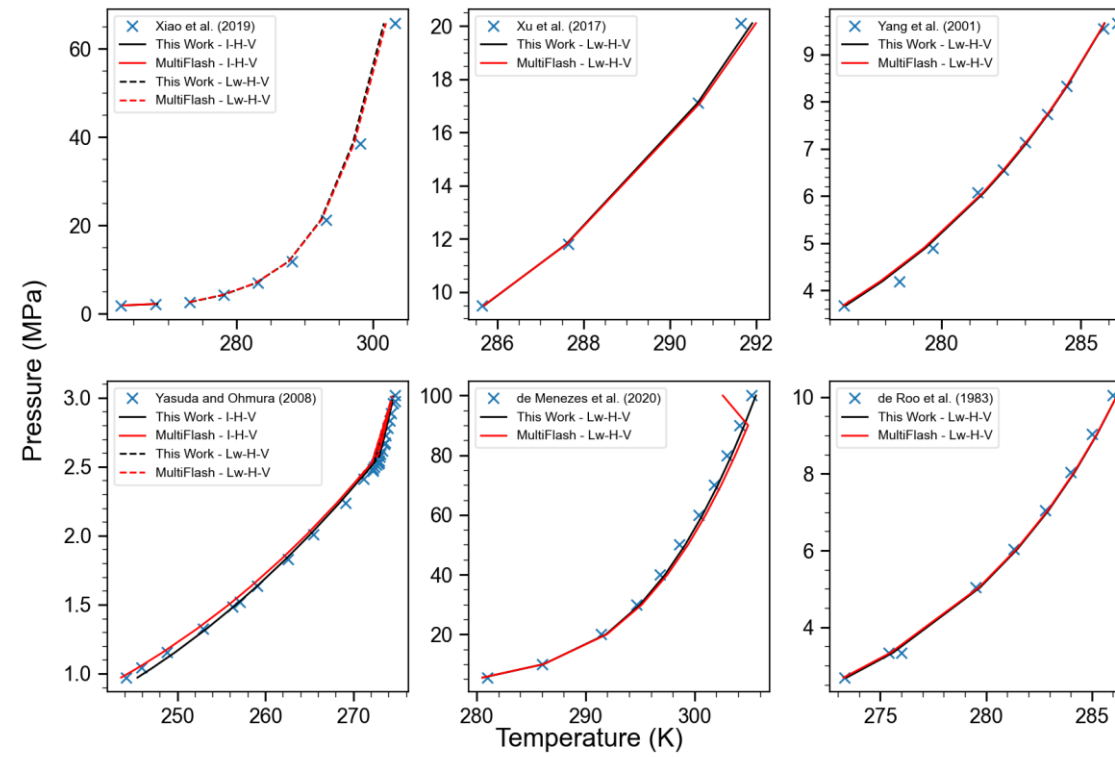


Figure S7: Selected hydrate equilibrium datasets (group 7) for simple CH₄ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{14,15,62–65}

3.1.2. C₂H₆ simple hydrate equilibria

Table S10: Database of C₂H₆ simple hydrate equilibrium data, with comparison of the AADT of the cavity-based model against CPAHYD-MF and B&S. Data types: "Tr" = Training Data; "Te" = Test Data.

Reference	Phases	AA DT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N	Type
Avlonitis (1988) ⁶⁸	Lw-H-V	0.101	0.505	0.155	277.8	287.2	0.848	3.082	10	Tr
Clarke and Bishnoi (2001) ¹³	Lw-H-V	0.884	0.457	0.736	274.15	280.65	0.487	1.087	7	Te
de Menezes et al. (2020) ¹⁴	Lw-H-V	0.380	0.978	0.379	286.16	298.09	3	90	12	Tr
Deaton and Frost (1946) ¹⁶	Lw-H-V	0.078	0.358	0.061	273.7	286.5	0.503	2.73	20	Tr
	I-H-V	0.108	1.016	0.476	263.6	272	0.313	0.457	4	Tr
Englezos and Bishnoi (1991) ⁶⁹	Lw-H-V	0.057	0.376	0.051	274.3	282.98	0.548	1.637	6	Te
Falabella and Vanpee (1974) ⁷⁰	I-H-V	2.757	0.537	0.308	200.8	240.8	0.0083	0.1013	5	Te
Galloway et al. (1970) ²⁰	Lw-H-V	0.144	0.300	0.013	277.6	292.5	0.814	1.551	3	Te
Hashimoto et al. (2008) ⁷¹	Lw-H-V	0.192	0.370	0.270	279.1	288.1	1.01	3.32	3	Tr
Holder and Grigoriou (1980) ⁷²	Lw-H-V	0.304	0.238	0.262	277.5	286.5	0.78	2.62	7	Te
Holder and Hand (1982) ⁷³	Lw-H-V	0.186	0.281	0.204	278.8	288.2	0.95	3.36	8	Te
	Lw-H-V-LHC	0.603	0.266	0.687	288.3	288.3	3.33	3.33	2	Te
Long et al. (2010) ⁷⁴	Lw-H-V	0.187	0.230	0.144	280.1	285.6	1.11	2.32	5	Tr
Maekawa (2012) ⁷⁵	Lw-H-V	0.049	0.368	0.047	276.6	287.5	0.73	3.22	9	Tr
Matsui et al. (2010) ⁷⁶	Lw-H-V	0.096	0.325	0.033	274.15	284.15	0.53	1.913	3	Tr
Mohammadi and Richon (2010) ⁷⁷	I-H-V	0.315	0.750	0.414	262.5	272.2	0.29	0.462	4	Tr
Mohammadi et al. (2008a) ⁷⁸	Lw-H-V	0.323	0.112	0.214	275.2	282.1	0.6	1.4	3	Tr
Morita et al. (2000) ⁷⁹	Lw-H-LHC	0.238	0.793	0.360	298.01	299.15	89	99	2	Te
Nakano et al. (1998a) ⁸⁰	Lw-H-LHC	0.205	0.549	0.347	290.42	298.36	19.48	83.75	26	Tr
Ng and Robinson (1985) ⁸¹	Lw-H-LHC	0.135	0.359	0.149	288	290.6	3.33	20.34	8	Te
Ng et al. (1983) ⁸²	Lw-H-V	0.115	0.374	0.148	288	290.63	3.33	20.34	8	Te
Nixdorf and Oellrich (1997) ⁴⁶	Lw-H-V	0.141	0.271	0.075	273.68	287.61	0.499	3.244	15	Tr
Reamer et al. (1952) ⁸³	Lw-H-V	0.432	0.598	0.380	279.9	287.4	0.972	3.298	4	Te
Roberts et al. (1940) ⁵⁰	Lw-H-LHC	0.206	0.420	0.217	287.7	288.4	3.413	6.84	9	Te
	Lw-H-V	0.349	0.758	0.401	273.4	287	0.545	3.054	11	Te
	I-H-V	1.379	2.372	1.856	260.8	269.3	0.29	0.441	3	Te
Yasuda and Ohmura (2008) ⁶⁵	I-Lw-H-V*	0.438	0.343	0.061	267.2	275.9	0.359	0.658	21	Tr
	Lw-H-V	0.245	0.074	0.084	273.9	275.7	0.508	0.637	2	Tr

Reference	Phases	ADT (K)	CPAHYD-MF ADT (K)	B&S ADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N	Type
	I-Lw-H-V	0.702	0.182	0.129	273.1	273.1	0.463	0.463	1	Tr
	I-H-V	0.517	0.402	0.388	244.9	271.9	0.122	0.443	10	Tr
Training	—	0.237	0.458	0.197	244.9	298.36	0.122	90	148	—
Test	—	0.477	0.513	0.342	200.8	299.15	0.0083	99	83	—
Overall	—	0.366	0.518	0.292	200.8	299.15	0.0083	99	231	—

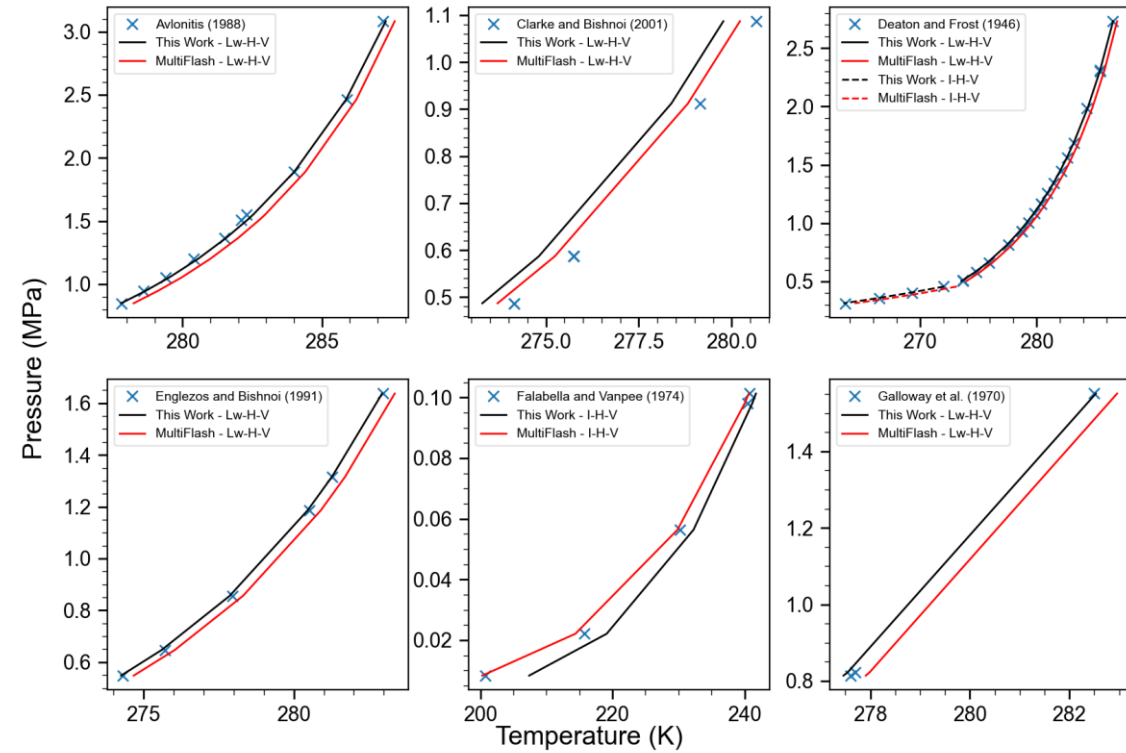


Figure S8: Selected hydrate equilibrium datasets (group 1) for simple ethane hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets: ^{13,16,20,68-70}

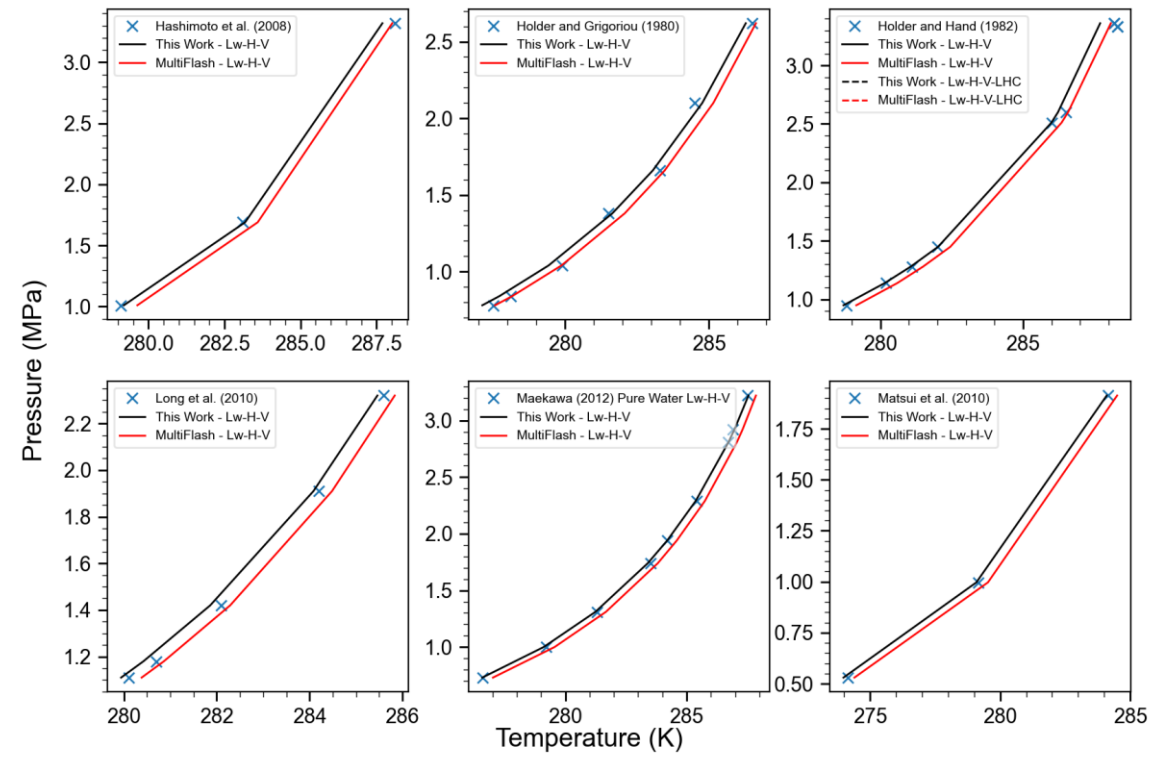


Figure S9: Selected hydrate equilibrium datasets (group 2) for simple ethane hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{71–76}

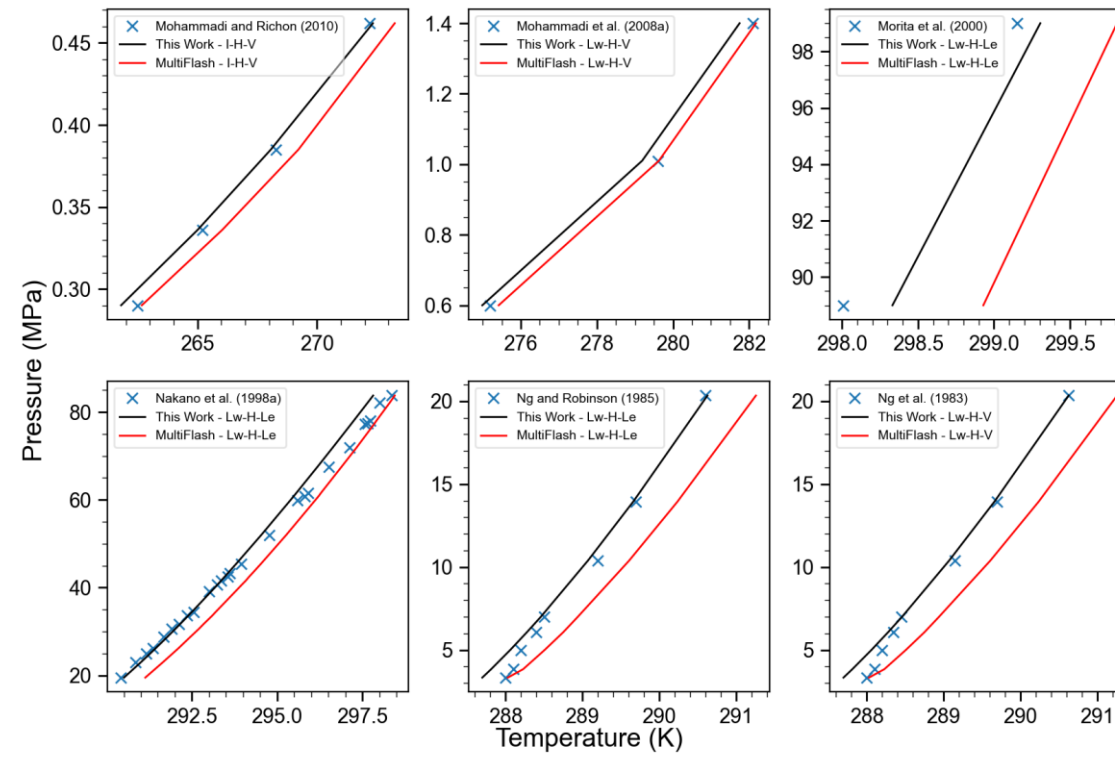


Figure S10: Selected hydrate equilibrium datasets (group 3) for simple ethane hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{77–82}

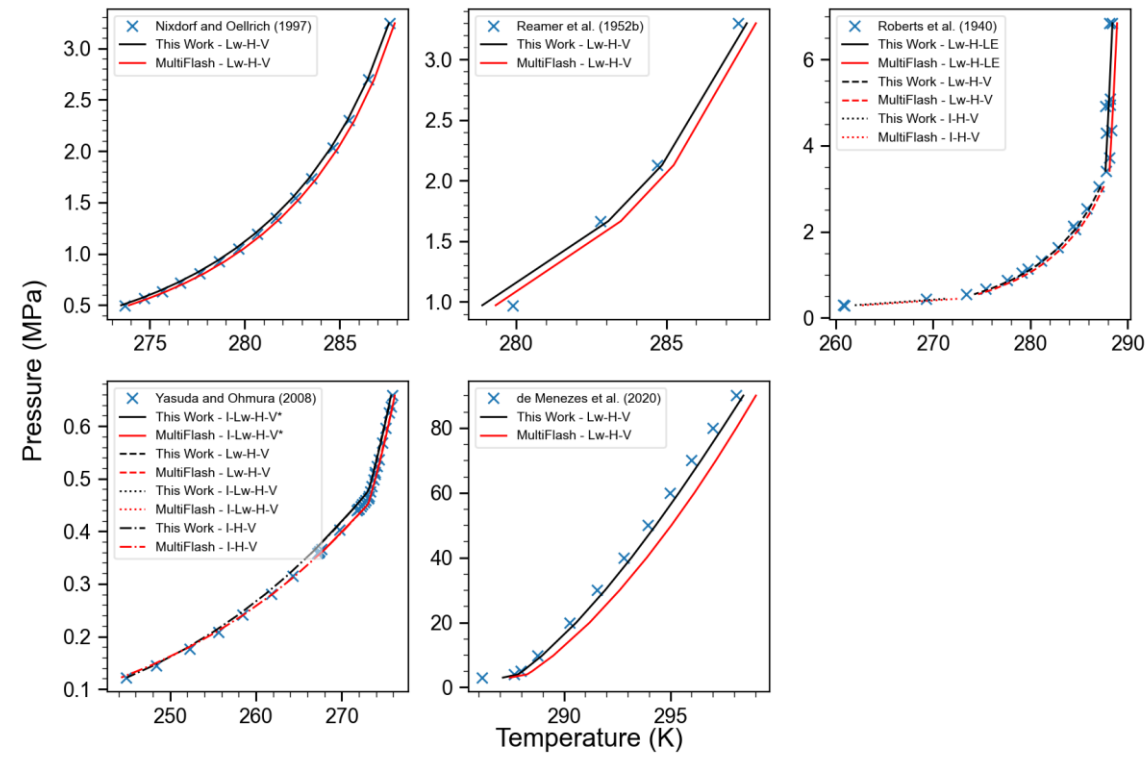


Figure S11: Selected hydrate equilibrium datasets (group 4) for simple ethane hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets: ^{14,46,50,65,83}

3.1.3. CO₂ simple hydrate equilibria

Table S11: Database of simple CO₂ hydrate equilibrium data, with comparison of the AADT of the cavity-based model against CPAHYD-MF and B&S. Data types: "Tr" = Training Data; "Te" = Test Data.

Reference	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N	Type
Adisasmito et al. (1991) ⁸	Lw-H-V	0.159	0.173	0.102	274.3	282.9	1.42	4.37	9	Tr
Chen et al. (2009) ¹²	Lw-H-V	0.181	0.222	0.045	275.25	279.85	1.59	2.86	4	Te
Chima-Maceda et al. (2019) ⁸⁴	Lw-H-V	0.108	0.090	0.255	276.22	282.54	1.74	4.09	5	Tr
Dai et al. (2020) ⁸⁵	Lw-H-V	0.117	0.093	0.334	275.65	283.25	1.616	4.452	11	Tr
de Menezes et al. (2020) ¹⁴	Lw-H-V	0.081	0.694	0.199	283.7	288.45	9.8	80	8	Tr
Deaton and Frost (1946) ¹⁶	Lw-H-V	0.145	0.158	0.137	273.7	282.9	1.324	4.323	19	Te
Dholabhai et al. (1993) ⁸⁶	Lw-H-V	0.112	0.154	0.032	273.8	279	1.34	2.52	4	Te
Fan and Guo (1999) ⁸⁷	LHC-H-Lw	0.713	0.791	0.400	283.1	283.6	9.32	12.87	3	Te
Fan and Guo (1999) ⁸⁷	Lw-H-V	0.194	0.196	0.142	273.6	282	1.31	4.02	9	Te
Fan et al. (2000) ⁸⁸	Lw-H-LHC	0.286	0.269	0.124	283.33	283.36	5.97	7.35	2	Te
Fan et al. (2000) ⁸⁸	Lw-H-V-LHC	0.090	0.011	0.385	283.27	283.27	4.48	4.48	1	Te
Fan et al. (2000) ⁸⁸	Lw-H-V	0.184	0.174	0.363	274.7	282.5	1.5	4.01	13	Te
Ferrari et al. (2016) ⁸⁹	Lw-H-V	0.023	0.046	0.242	275.65	281.65	1.65	3.5	5	Te
Hachikubo et al. (2002) ²³	Lw-H-V	0.176	0.181	0.198	273.93	278.05	1.349	2.204	4	Te
Hachikubo et al. (2002) ²³	I-H-V	0.778	0.224	0.214	263.17	271.23	0.774	1.029	3	Te
Ilani-Kashkouli et al. (2016) ⁹⁰	Lw-H-V	0.075	0.091	0.294	279.3	283.3	2.57	4.45	4	Tr
Jarrhian and Nakhaee (2019) ⁹¹	Lw-H-V	0.059	0.089	0.125	274.15	280.15	1.39	2.91	7	Te
Kamari et al. (2017) ³¹	Lw-H-V	0.211	0.229	0.123	277.2	281.9	2.04	3.69	4	Tr
Khan et al. (2017) ⁹²	Lw-H-V	0.392	0.388	0.687	277.4	283	1.85	3.95	5	Tr
Komai et al. (1997) ³⁴	Lw-H-V	0.722	0.709	1.009	278.15	283.05	1.9	4.1	3	Te
Larson (1955) ⁹³	Lw-H-V	0.225	0.157	0.240	271.8	283.2	1.048	4.502	36	Te
Lee et al. (2012) ⁹⁴	Lw-H-V	0.239	0.281	0.126	274	278	1.41	2.23	2	Tr
Maekawa (2010) ⁹⁵	Lw-H-V	0.173	0.184	0.136	273.6	283.1	1.33	4.54	13	Tr
Mannar et al. (2017) ⁹⁶	Lw-H-V	0.205	0.208	0.473	276.65	282.7	1.87	3.78	5	Tr
Matsui et al. (2010) ⁷⁶	Lw-H-V	0.065	0.080	0.109	274.15	279.15	1.385	2.543	2	Tr
Melnikov et al. (2011) ⁹⁷	Lw-H-V	0.170	0.153	0.249	273.3	280.2	1.25	2.95	6	Tr
Mohammadi (2018) ⁹⁸	Lw-H-V	0.101	0.077	0.298	277.8	281.9	2.1	3.67	6	Tr
Mohammadi and Richon (2011) ⁹⁹	I-H-V	0.860	0.433	0.160	260.2	270.7	0.682	1.003	5	Tr

Reference	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N	Type
Mohammadi et al. (2005) ⁴²	Lw-H-V	0.109	0.091	0.242	277.5	282.5	2.048	4.02	6	Tr
Nema et al. (2017) ¹⁰⁰	Lw-H-V	0.194	0.111	0.059	271.65	275.75	1.056	1.708	7	Tr
Ng and Robinson (1983) ⁸²	Lw-H-LCO2	0.575	0.605	0.213	282.92	283.93	5.03	14.36	6	Tr
Ng and Robinson (1983) ⁸²	Lw-H-V	0.402	0.375	0.068	279.59	282.79	2.74	4.36	3	Tr
Ohgaki et al. (1993) ¹⁰¹	H-Lw-LHC	1.337	1.312	1.032	281.14	283.59	4.386	8.93	8	Te
Ohgaki et al. (1993) ¹⁰¹	Lw-LHC-V	2.191	2.231	2.552	283.07	289.37	4.485	5.216	10	Te
Ohgaki et al. (1993) ¹⁰¹	Lw-H-V	0.630	0.653	0.444	273.36	281.79	1.338	4.085	32	Te
Ohgaki et al. (1996) ⁴⁷	Lw-H-V	0.354	0.371	0.030	280.3	280.3	3.04	3.04	1	Te
Robinson and Mehta (1971) ¹⁰²	Lw-H-V-LHC	0.044	0.034	0.430	283.3	283.3	4.468	4.468	1	Te
Robinson and Mehta (1971) ¹⁰²	Lw-H-V	0.149	0.147	0.136	273.9	282	1.379	3.84	6	Te
Ruffine and Trusler (2010) ¹⁰³	Lw-H-V	0.205	0.210	0.337	275.03	282.76	1.502	4.079	10	Tr
Ruffine and Trusler (2010) ¹⁰³	Lw-H-LHC	0.303	0.391	0.298	283.25	286.76	5.993	46.575	3	Tr
Ruffine and Trusler (2010) ¹⁰³	Lw-H-V-LHC	0.441	0.366	0.030	282.85	282.85	4.43	4.43	1	Tr
Sabil et al. (2010) ¹⁰⁴	Lw-H-V	0.189	0.156	0.425	275.12	282.9	1.51	4.3	10	Tr
Sabil et al. (2014) ⁵²	Lw-H-V	0.166	0.153	0.276	272.65	281.45	1.1	3.38	11	Tr
Sami et al. (2013) ⁵⁴	Lw-H-V	0.209	0.206	0.265	276.7	281.57	1.82	3.76	5	Te
Seif et al. (2018) ¹⁰⁵	Lw-H-V	0.532	0.497	0.296	280.3	283.1	3.21	4.54	2	Te
Seo et al. (2000) ¹⁰⁶	Lw-H-V	0.177	0.206	0.051	274.76	281.46	1.5	3.5	4	Tr
Servio et al. (2001) ¹⁰⁷	Lw-H-V	1.613	2.933	3.039	277.05	283.15	2	4.2	9	Te
Sun et al. (2016) ¹⁰⁸	Lw-H-V	0.119	0.166	0.082	276.15	278.15	1.747	2.296	9	Tr
Takenouchi and Kennedy (1965) ¹⁰⁹	Lw-H-LHC	0.175	0.399	0.126	283.2	289.2	4.5	88.1	9	Te
Unruh and Katz (1949) ¹¹⁰	Lw-H-V-LHC	0.291	0.214	0.187	283.1	283.1	4.502	4.502	1	Te
Unruh and Katz (1949) ¹¹⁰	Lw-H-V	0.206	0.225	0.129	277.2	281.9	2.041	3.689	4	Te
Vlahakis et al. (1972) ¹¹¹	Lw-H-V	0.192	0.119	0.155	271.6	283.2	1.04	4.509	44	Tr
Wendland et al. (1999) ¹¹²	Lw-H-V	0.161	0.173	0.115	273.93	282.16	1.365	3.85	7	Te
Yasuda and Ohmura (2008) ⁶⁵	I-H-V	0.675	0.132	0.489	244.5	269.4	0.364	0.963	10	Tr
Yasuda and Ohmura (2008) ⁶⁵	Lw-H-V	0.156	0.119	0.222	273.8	275.7	1.312	1.628	2	Tr
Yasuda and Ohmura (2008) ⁶⁵	I-Lw-H-V*	0.884	0.466	0.392	267.8	275	0.899	1.501	21	Tr
Yasuda and Ohmura (2008) ⁶⁵	I-Lw-H-V	1.567	0.815	0.482	271.7	271.7	1.03	1.03	1	Tr
Yoon and Lee (1997) ¹¹³	Lw-H-V	0.101	0.064	0.329	275.4	282.4	1.56	3.89	4	Te
Yu et al. (2016) ¹¹⁴	Lw-H-V	0.158	0.184	0.076	275.7	279.7	1.641	2.761	5	Tr
Zha et al. (2012) ¹¹⁵	Lw-H-V	0.071	0.078	0.264	274.42	282.83	1.47	4.15	5	Tr
Training	—	0.285	0.220	0.246	244.5	288.45	0.364	80	243	—

Reference	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N	Type
Test	—	0.470	0.524	0.511	263.17	289.37	0.774	88.1	212	—
Overall	—	0.371	0.362	0.370	244.5	289.37	0.364	88.1	455	—

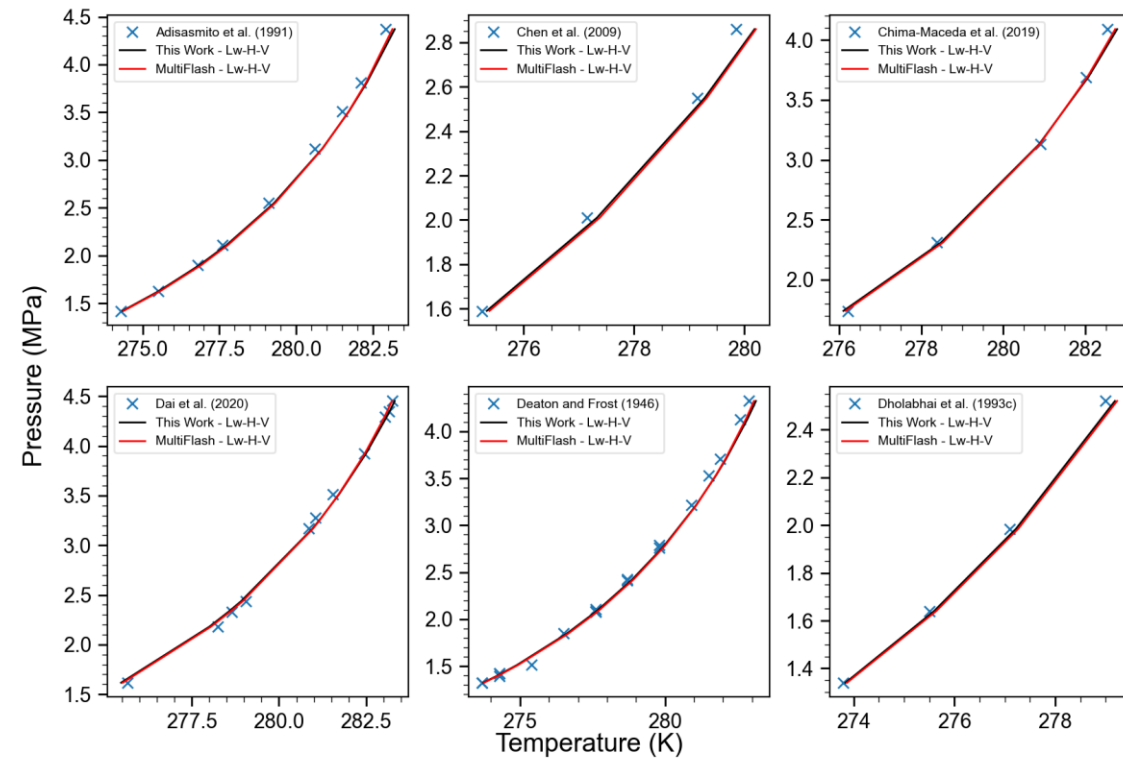


Figure S12: Selected hydrate equilibrium datasets (group 1) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{8,12,16,84–86}

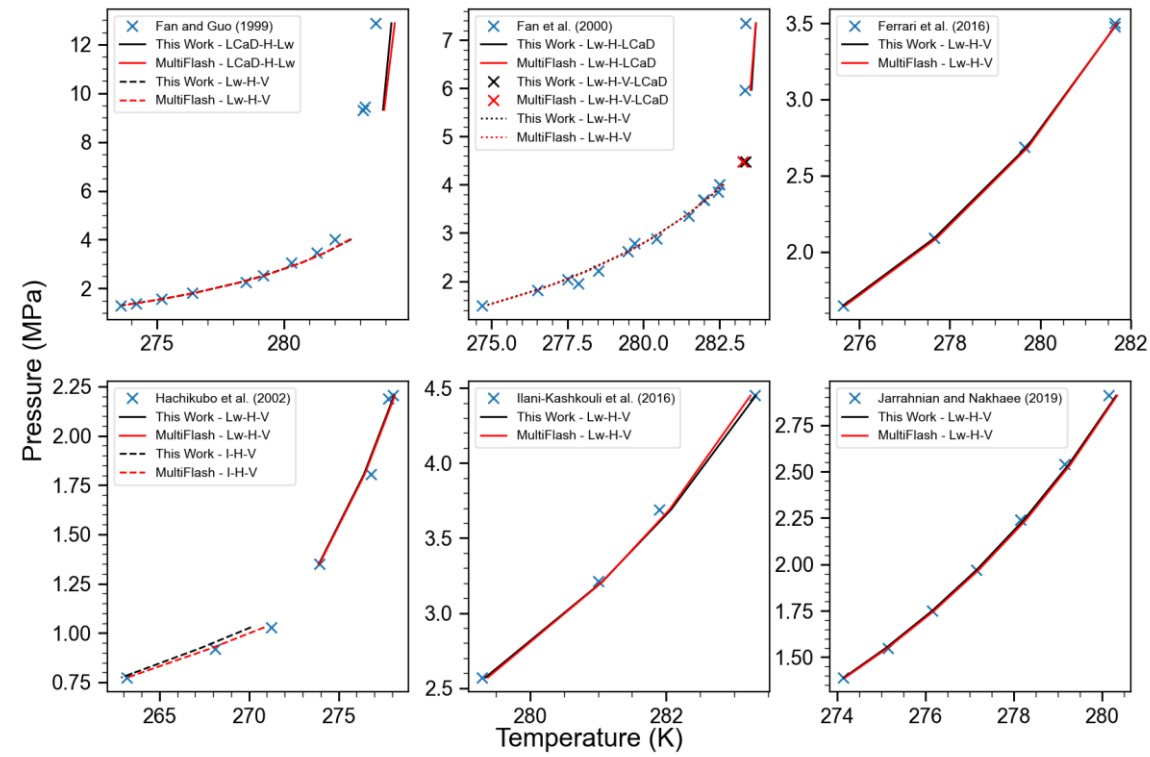


Figure S13: Selected hydrate equilibrium datasets (group 2) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{23,87-91}

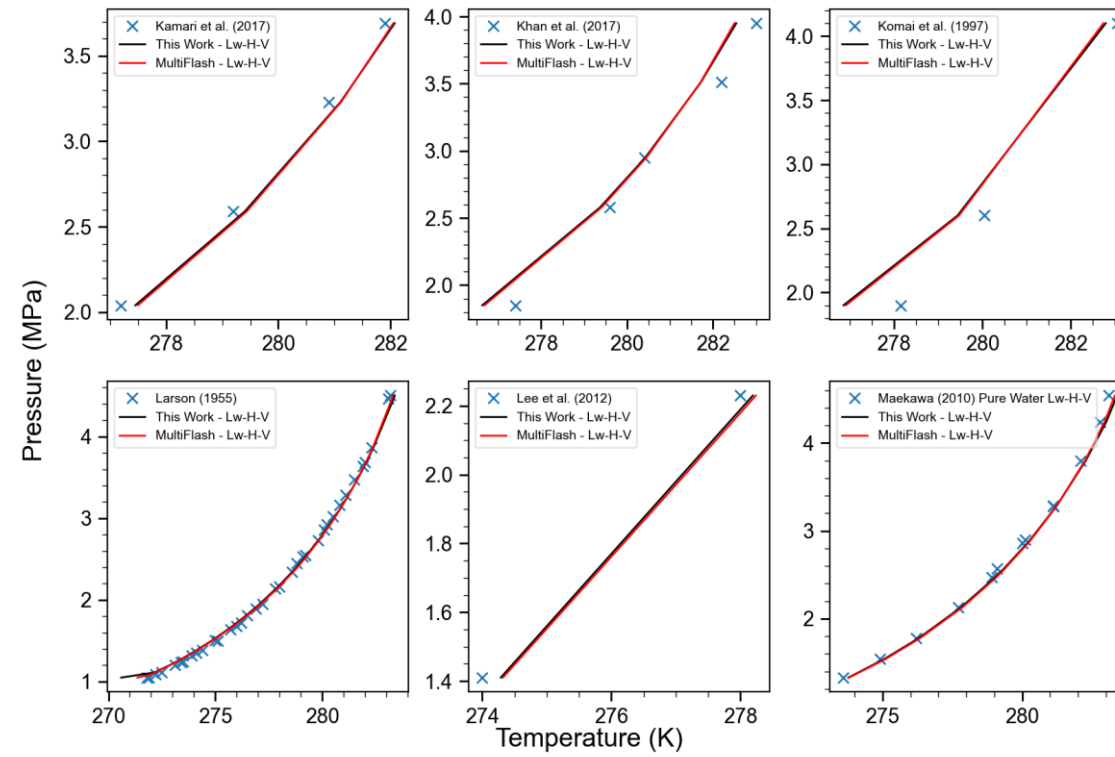


Figure S14: Selected hydrate equilibrium datasets (group 3) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{31,34,92-95}

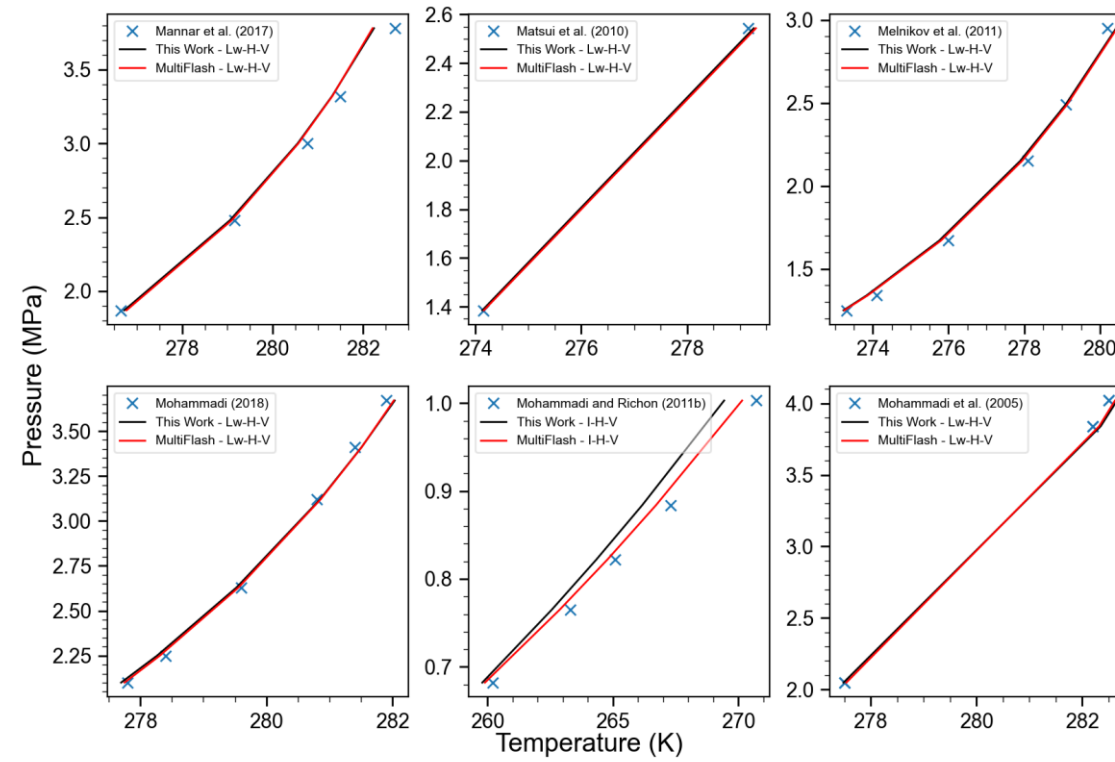


Figure S15: Selected hydrate equilibrium datasets (group 4) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{42,76,96-99}

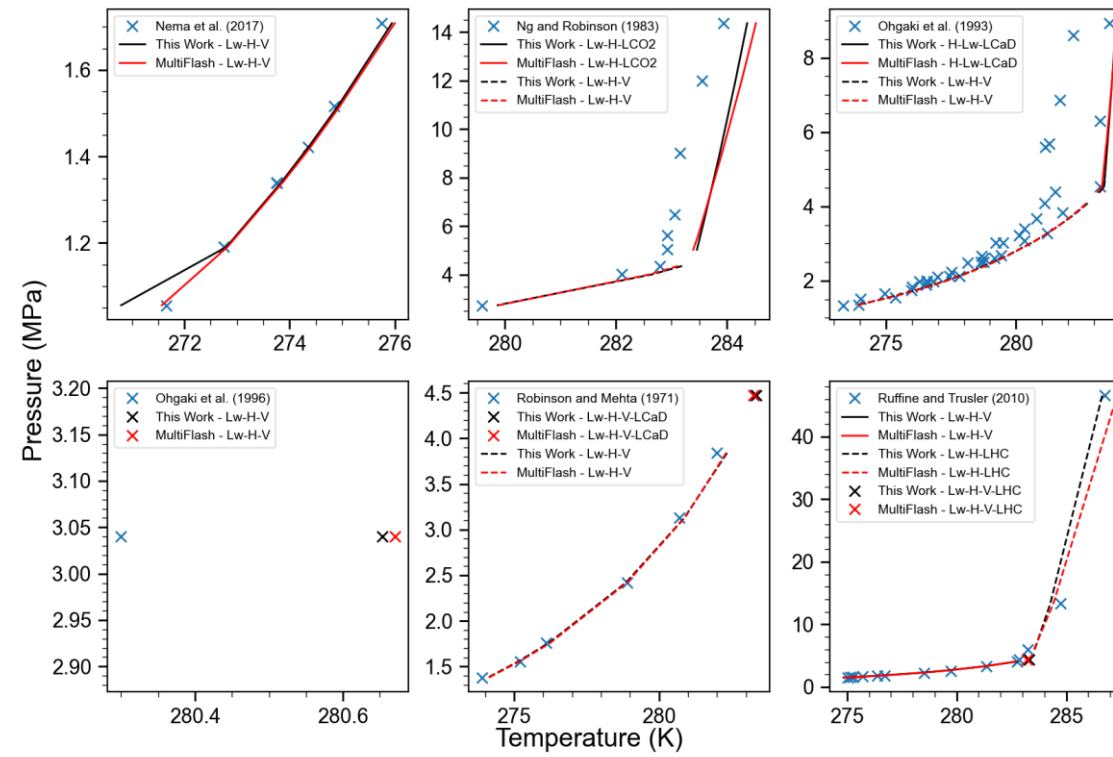


Figure S16: Selected hydrate equilibrium datasets (group 5) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{47,82,100-103}

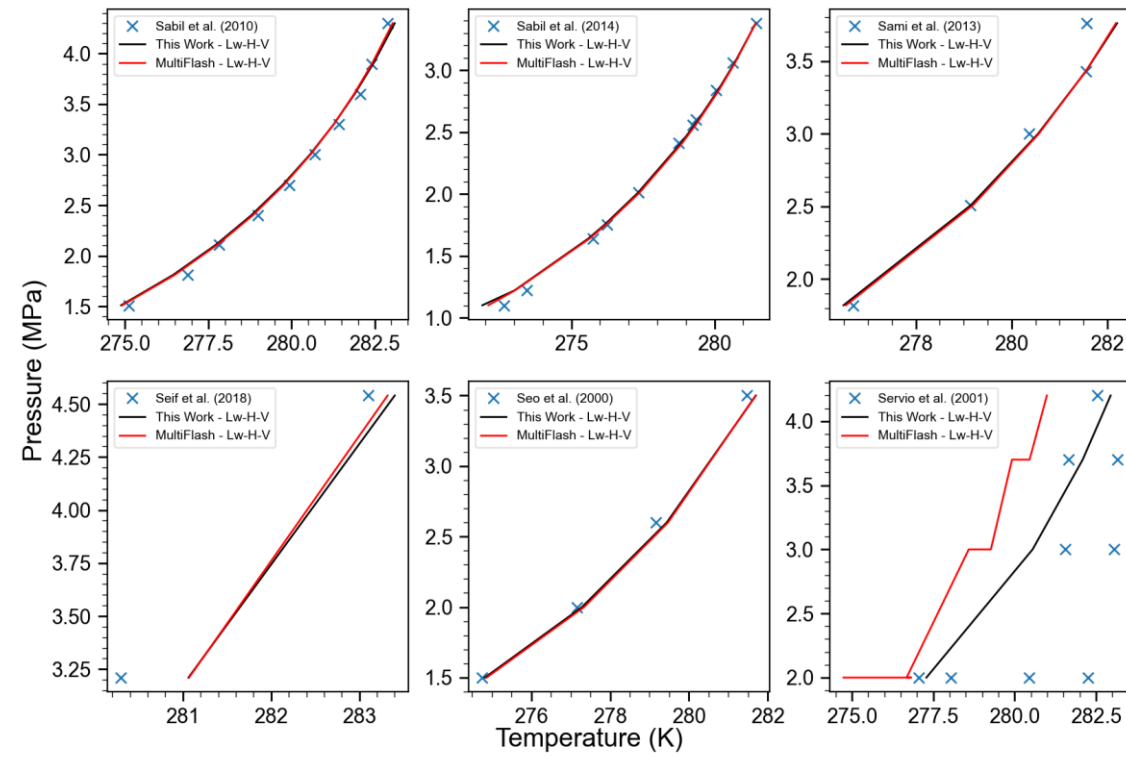


Figure S17: Selected hydrate equilibrium datasets (group 6) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{52,54,104-107}

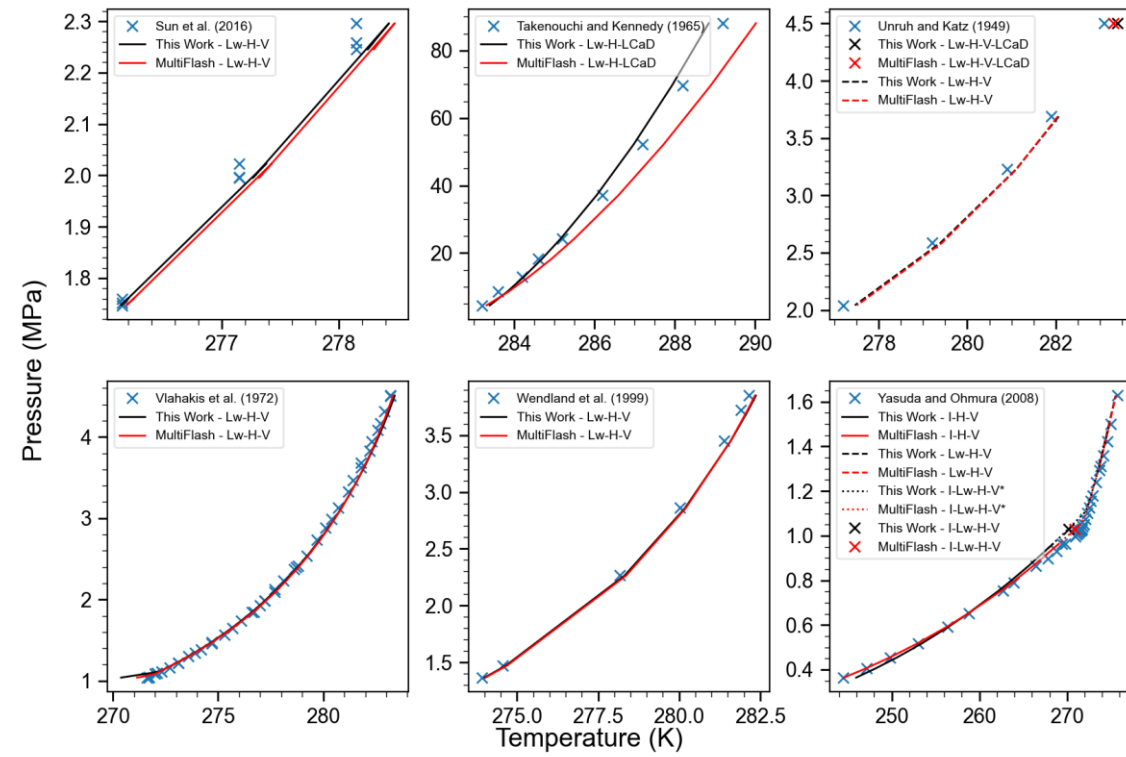


Figure S18: Selected hydrate equilibrium datasets (group 7) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{65,108–112}

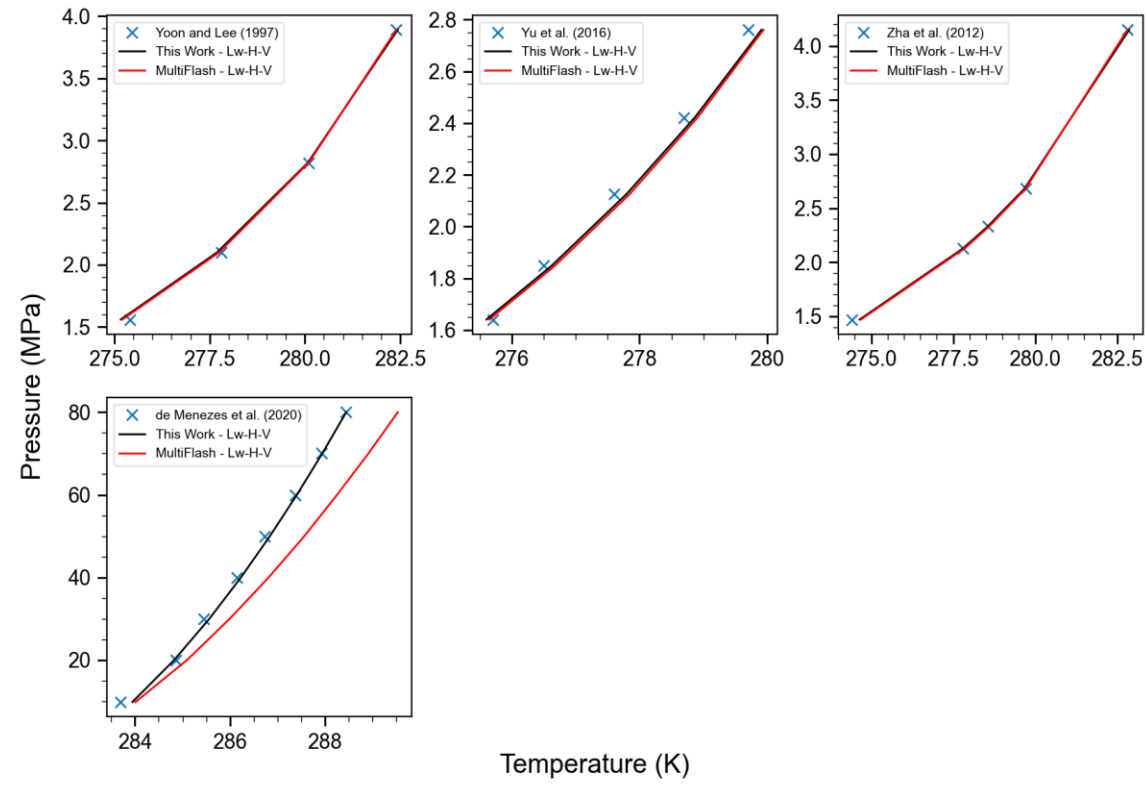


Figure S19: Selected hydrate equilibrium datasets (group 8) for simple CO₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{14,113–115}

3.1.4. C₃H₈ simple hydrate equilibria

Table S12: Database of C₃H₈ simple hydrate phase equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data. In the phases type, I-Lw-H-V* refers to measurements very close to the quadruple point (just above or below in temperature)

Reference	Phases	AA DT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N	Type
Holder and Godbole (1982) ⁷³	I-H-V	1.104	0.673	2.406	247.9	262.1	0.0482	0.0994	8	Tr
Kubota et al. (1984) ¹¹⁶	Lw-H-V	0.190	0.219	0.185	274.2	278.4	0.207	0.542	9	Te
Maekawa (2008) Pure Water ¹¹⁷	Lw-H-V	0.181	0.201	0.202	274.2	278.1	0.211	0.509	12	Tr
Mohammadi et al. (2008a) ⁷⁸	Lw-H-V	0.335	0.364	0.096	274.6	278.3	0.22	0.5	3	Te
Mooijer-van den Heuvel et al. (2002) ¹¹⁸	Lw-H-V	0.264	0.297	0.144	276.77	278.55	0.368	0.547	9	Tr
	Lw-H-V-LHC	0.288	0.376	0.117	278.62	278.62	0.6	0.6	1	Tr
	Lw-H-LHC	0.536	0.569	0.023	278.71	278.89	0.643	9.893	17	Tr
Nixdorf and Oellrich (1997) ⁴⁶	Lw-H-V	0.071	0.103	0.337	273.55	278.52	0.186	0.567	10	Tr
Patil (1987) ¹¹⁹	Lw-H-V	0.144	0.170	0.443	273.6	278	0.207	0.51	5	Te
Reamer et al. (1952) ⁸³	Lw-H-V	0.163	0.181	0.448	274.3	277.2	0.241	0.414	3	Te
	Lw-H-LHC	0.382	0.457	0.076	278.6	278.8	0.684	2.046	3	Te
Robinson and Mehta (1971) ¹⁰²	Lw-H-V	0.298	0.312	0.093	274.3	277.8	0.207	0.455	4	Te
	Lw-H-V-LHC	0.606	0.674	0.504	278.9	278.9	0.552	0.552	1	Te
Thakore and Holder (1987) ⁵⁹	Lw-H-V	0.242	0.253	0.255	274.2	278.2	0.217	0.51	7	Te
Verma (1974) ⁶⁰	Lw-H-V,Lw-H-LHC	0.265	0.282	0.122	273.9	278	0.188	0.512	8	Tr
	Lw-H-V-LHC	0.317	0.298	0.336	278.4	278.6	0.562	16.8	5	Te
Yasuda and Ohmura (2008) ⁶⁵	I-H-V	1.047	0.598	2.310	245	272.1	0.041	0.1627	10	Tr
	Lw-H-V	0.217	0.215	0.191	273.9	275.5	0.194	0.28	2	Tr
	I-Lw-H-V*	0.360	0.254	0.851	267.8	276	0.131	0.309	25	Tr
	I-Lw-H-V	0.490	0.351	0.277	273.2	273.2	0.17	0.17	1	Tr
Training	—	0.447	0.358	0.707	245	278.89	0.041	9.893	103	—
Test	—	0.254	0.275	0.252	273.6	278.9	0.207	16.8	40	—
Overall	—	0.393	0.335	0.580	245	278.9	0.041	16.8	143	—

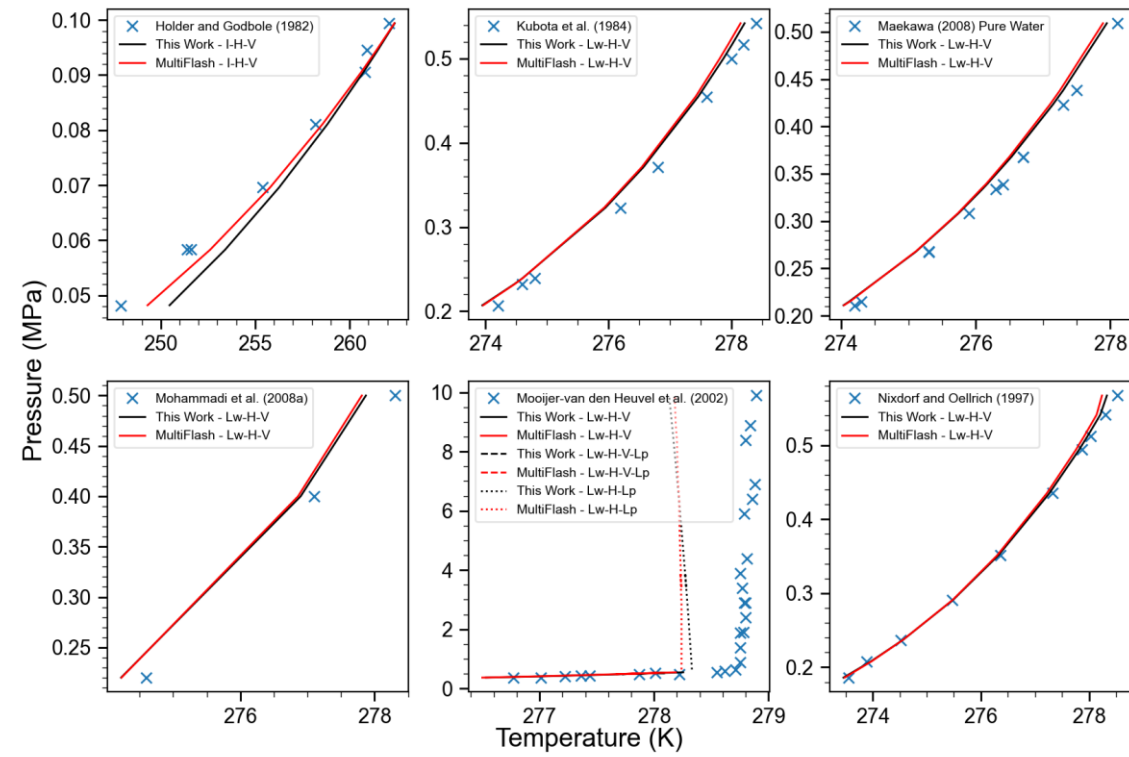


Figure S20: Selected hydrate equilibrium datasets (group 1) for simple propane hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{46,73,78,116-118}

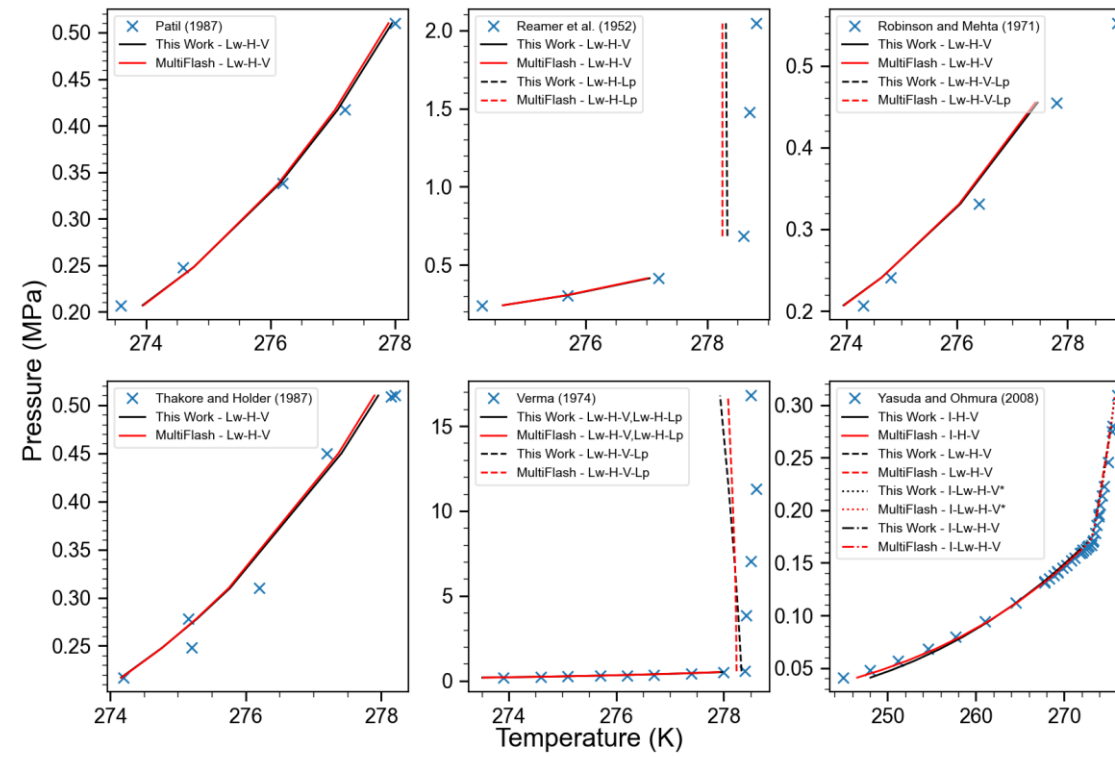


Figure S21: Selected hydrate equilibrium datasets (group 2) for simple propane hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets: ^{59,60,65,83,102,119}

3.1.5. N₂ simple hydrate equilibria

Table S13: Database of N₂ simple hydrate equilibrium data, with comparison of the AADT of the cavity-based model with CPAHYD-MF and B&S. Data types: 'Tr' = Training Data; 'Te' = Test Data.

Reference	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N	Type
Jarrahan and Nakhaee (2019) ⁹¹	Lw-H-V	0.124	0.187	0.067	274.15	280.15	17.95	32.91	7	Tr
Jhaveri and Robinson (1965) ³⁰	Lw-H-V	0.190	0.206	0.164	273.2	281.1	16.27	35.16	8	Tr
Lee et al. (2014) ¹²⁰	Lw-H-V	0.304	0.283	0.326	273	277.5	16.13	23.9	7	Tr
Marshall et al. (1964) ³⁹	Lw-H-V	0.133	0.325	0.097	277.6	291.6	24.93	101.98	4	Te
Mohammadi and Richon (2010) ⁷⁷	I-H-V	0.301	1.029	1.143	261.7	270.2	11.25	13.8	6	Tr
Mohammadi et al. (2003) ⁴¹	Lw-H-V	0.262	0.371	0.171	274.55	283.05	19.093	45.355	3	Te
Nixdorf and Oelrich (1997) ⁴⁶	Lw-H-V	0.047	0.023	0.083	273.67	277.27	16.935	24.092	5	Te
Sugahara et al. (2002) ¹²¹	Lw-H-V	0.654	0.134	0.473	285.63	291.96	55	101	5	Te
van Cleeff and Diepen (1960) ¹²²	Lw-H-V	0.301	1.029	1.143	261.7	270.2	11.25	13.8	6	Tr
Yasuda et al. (2013) I-H-V ¹²³	I-H-V	0.454	2.157	1.960	244.05	266.55	7.151	12.613	7	Tr
Training	—	0.221	0.520	0.391	244.05	291	7.151	95.86	73	—
Test	—	0.284	0.188	0.217	273.67	291.96	16.935	101.98	17	—
Overall	—	0.233	0.457	0.358	244.05	291.96	7.151	101.98	90	—

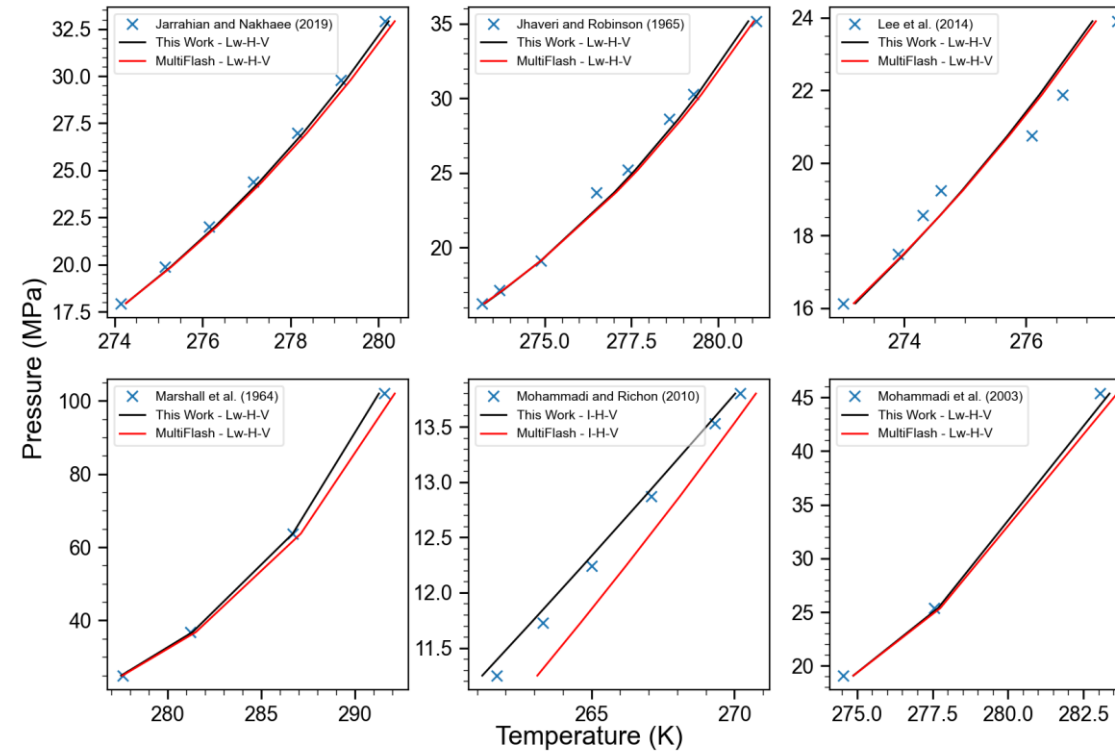


Figure S22: Selected hydrate equilibrium datasets (group 1) for simple N_2 hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{30,39,41,77,91,120}

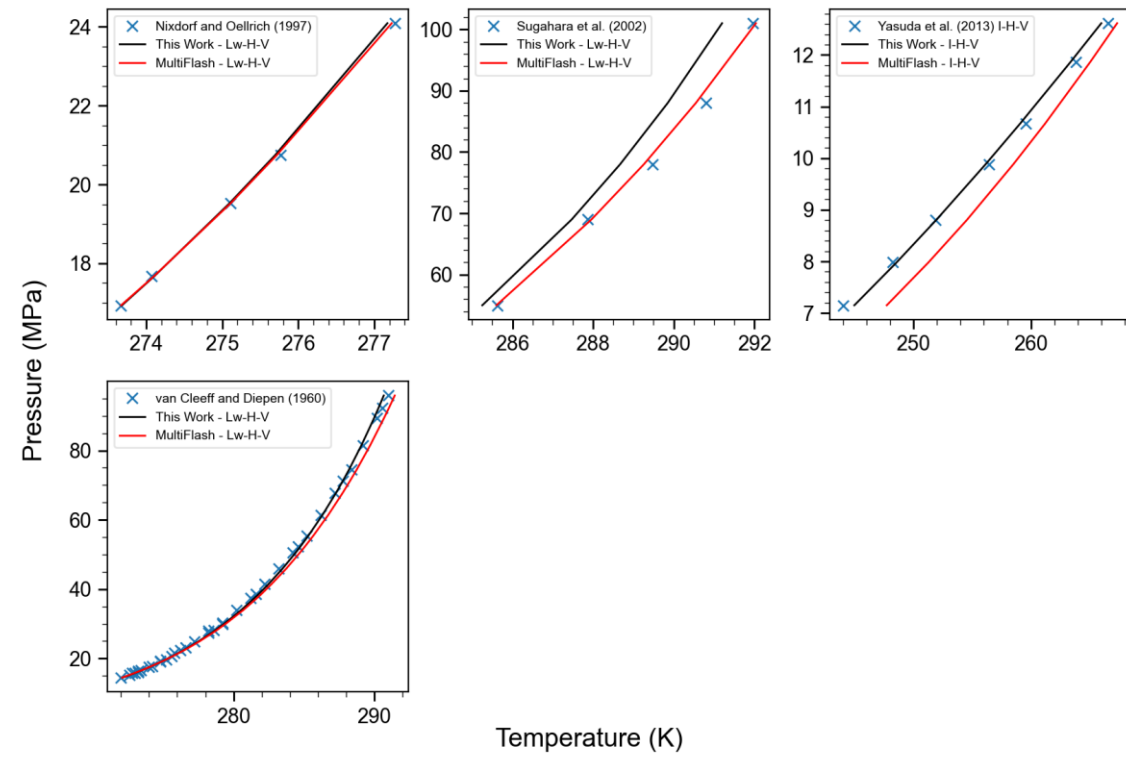


Figure S23: Selected hydrate equilibrium datasets (group 2) for simple N₂ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{46,121–123}

3.1.6. H₂S simple hydrate equilibria

Table S14: Database of H₂S simple hydrate equilibrium data, with comparison of the AADT of the cavity-based model with CPAHYD-MF and B&S. Data types: 'Tr' = Training Data; 'Te' = Test Data.

Reference	Phases	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N	Type
Adeniyi et al. (2018) ¹²⁴	Lw-H-V	0.338	0.323	0.379	285.23	302.44	0.36	2.234	14	Tr
	Lw-H-LHC	1.351	0.138	0.074	302.72	304.04	2.401	16.343	13	Te
Bond and Russell (1949) ¹²⁵	Lw-H-V	0.805	0.773	0.854	283.2	302.7	0.31	2.241	4	Te
Carroll and Mather (1991) ¹²⁶	LHC-H-V	1.241	2.818	1.818	298	302.6	2.03	2.24	19	Te
	Lw-H-V	1.105	1.122	1.161	298.6	300.8	1.61	2.07	13	Te
Mahadev and Bishnoi (1999) ¹²⁷	Lw-H-V	0.113	0.302	0.449	284.57	293.75	0.329	0.804	3	Tr
Mohammadi et al. (2009b) ¹²⁸	Lw-H-V	0.156	0.484	0.634	277.7	301.3	0.164	1.861	19	Tr
Selleck et al. (1952) ¹²⁹	I-Lw-H-V	1.811	0.563	0.365	272.8	272.8	0.093	0.093	2	Te
	Lw-H-V	0.509	0.435	0.511	272.8	302.1	0.093	2.068	12	Te
	Lw-H-V-LH2S	1.046	0.114	0.140	302.7	302.7	2.239	2.239	6	Te
	I-H-V	1.069	0.224	1.581	250.5	272.1	0.034	0.09	9	Te
	Lw-H-LH2S	1.608	0.055	0.134	302.8	305.4	3.447	35.068	15	Te
Ward et al. (2015) ⁶¹	Lw-H-V	0.199	0.204	0.398	273.68	301.53	0.1078	1.9598	61	Tr
Training	—	0.208	0.279	0.443	273.68	302.44	0.1078	2.234	97	—
Test	—	1.166	0.891	0.838	250.5	305.4	0.034	35.068	93	—
Overall	—	0.677	0.455	0.636	250.5	305.4	0.034	35.068	190	—

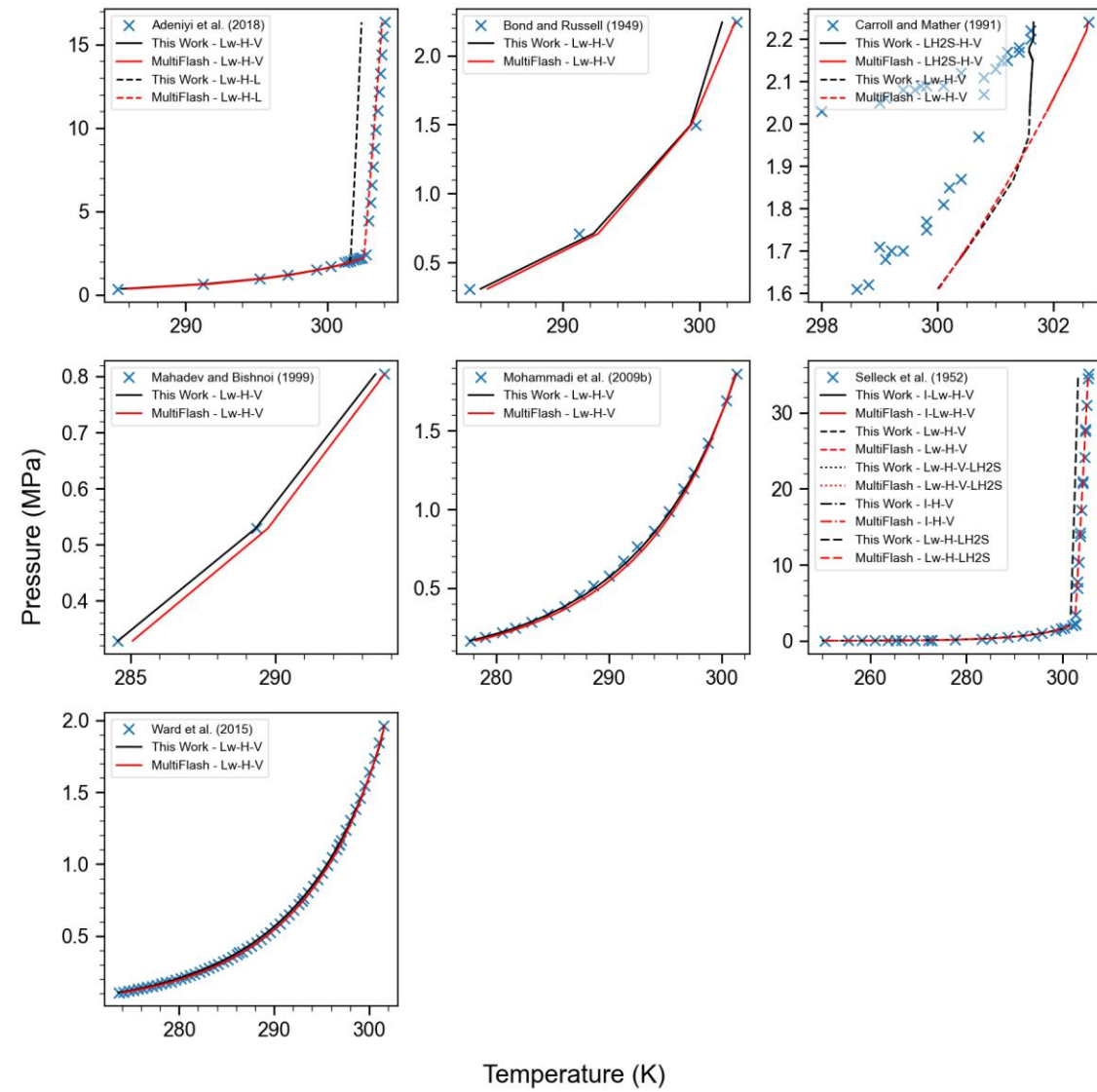


Figure S24: Selected hydrate equilibrium datasets for simple H_2S hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red).

Datasets: ^{61,124–127,129,130}

3.1.7. $i\text{-C}_4\text{H}_{10}$ simple hydrate equilibria

Table S15: Database of $i\text{-C}_4\text{H}_{10}$ simple hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N	Type
Holder and Godbole (1982) ⁷³	I-H-V	1.999	0.768	1.456	241.4	269.5	0.0176	0.0913	10	Te
Rouher and Barduhn (1969) ¹³¹	Lw-H-V	0.114	0.238	0.170	273.2	275	0.115	0.169	24	Tr
Schneider and Farrar (1968) ¹³²	I-H-V	0.545	0.599	0.557	271.2	275.1	0.095	0.109	7	Tr
	Lw-H-V	0.060	0.152	0.094	273.2	275.1	0.109	0.167	10	Tr
Thakore and Holder (1987) ⁵⁹	Lw-H-V	0.368	0.336	0.345	274.35	274.6	0.128	0.155	3	Tr
Wu et al. (1976) ¹³³	Lw-H-LHC	0.330	0.094	0.261	275.4	275.8	0.226	14.27	6	Tr
Training	—	0.205	0.260	0.230	271.2	275.8	0.095	14.27	50	—
Test	—	1.999	0.768	1.456	241.4	269.5	0.0176	0.0913	10	—
Overall	—	0.504	0.345	0.435	241.4	275.8	0.0176	14.27	60	—

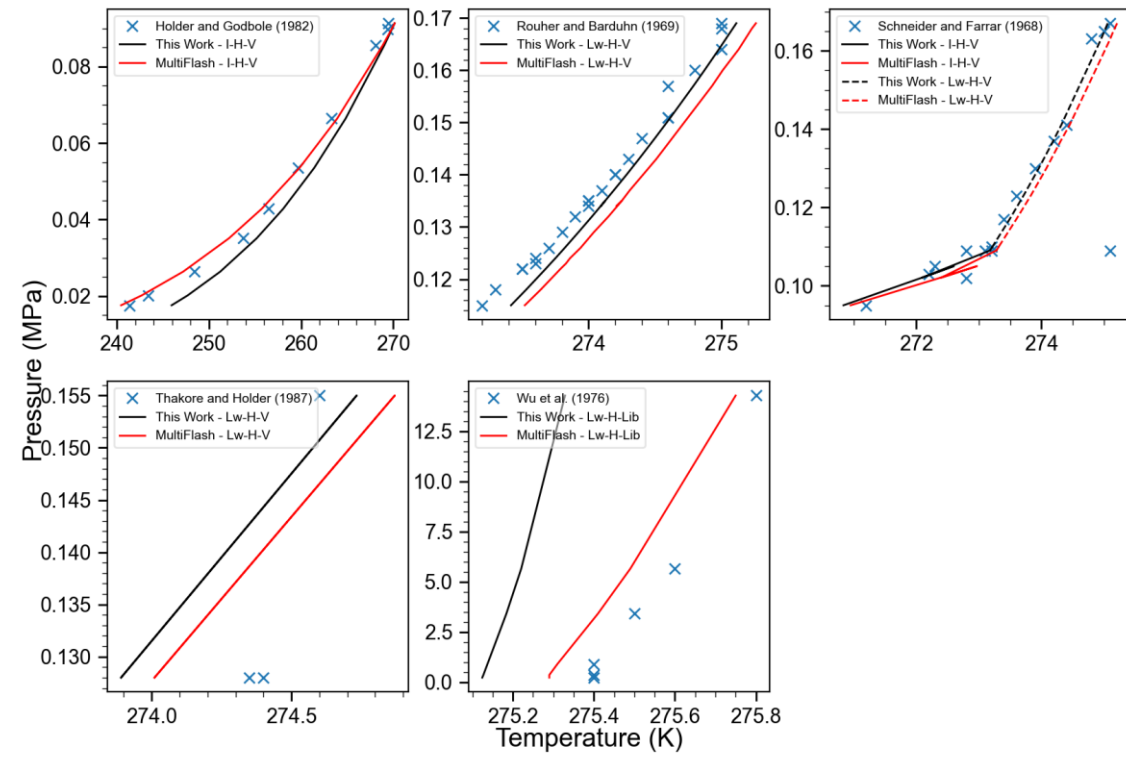


Figure S25: Selected hydrate equilibrium datasets for simple $i\text{-C}_4\text{H}_{10}$ hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red).

Datasets:^{59,73,131–133}

3.2. Binary-gas-hydrate equilibria

In these tables, two new columns, $x_{1,min}$ and $x_{1,max}$ are introduced, representing the range of the gaseous composition of component 1 for the binary-gas hydrate equilibrium data measured in the given reference. In all tables, the first component in the caption is component 1, and the second is component 2, where $x_1 + x_2 = 1$ for the water-free composition.

As some datasets are measured at fixed pressures and temperatures with varying gas composition, only those datasets that have a fixed gas composition with at least 3 measured PT points are plotted.

3.2.1. CH₄ + C₃H₈ binary- gas mixture hydrate equilibria

Table S16: Database of CH₄ and C₃H₈ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AA DT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Deaton and Frost (1946) ¹⁶	Lw-H-V	II	0.163	0.248	0.37544	274.8	283.2	0.272	4.358	0.3620	0.9900	25	Tr
Hemmingsen et al. (2011) ¹³⁴	Lw-H-V	II	0.292	0.220	0.413667	279.95	297.55	1.12	13.36	0.8813	0.8813	3	Tr
McLeod and Campbell (1961) ⁴⁰	Lw-H-V	II	0.141	0.248	0.650235	290.5	304.9	6.93	68.98	0.9450	0.9650	17	Tr
Nixdorf and Oelrich (1997) ⁴⁶	Lw-H-V	II	0.812	1.024	0.288286	278.09	297.53	1.416	24.363	0.9707	0.9707	7	Tr
Ovalle and Beltran (2021) ¹³⁵	Lw-H-V	II	0.529	0.818	0.35125	276.62	287.25	0.72	4.46	0.9000	0.9800	12	Te
Paranjpe et al. (1987) ¹³⁶	Lw-H-V-LHC	II	0.336	0.117	0.210667	279.2	281.2	0.674	0.832	0.0100	0.1110	3	Tr
Smith et al. (2017) ¹³⁷	Lw-H-V	II	0.363	0.325	1.30115	278.45	295.35	2.36	16.75	0.9597	0.9948	20	Tr
Thakore and Holder (1987) ⁵⁹	Lw-H-V	II	0.306	0.415	0.381179	275.15	278.15	0.245	1.306	0.0210	0.9560	28	Te
Verma et al. (1974) ⁶⁰	Lw-H-V	II	0.151	0.110	0.12525	274.4	282.3	0.263	0.945	0.0072	0.6510	12	Tr
	Lw-H-V-LHC	II	0.379	0.598	0.360617	279.6	300.2	0.66	17.49	0.0072	0.6510	60	Te
Training	—	—	0.266	0.304	0.596	274.4	304.9	0.263	68.98	0.0072	0.9948	87	—
Test	—	—	0.377	0.573	0.365	275.15	300.2	0.245	17.49	0.0072	0.9800	100	—
Overall	—	—	0.325	0.448	0.472631	274.4	304.9	0.245	68.98	0.0072	0.9948	187	—

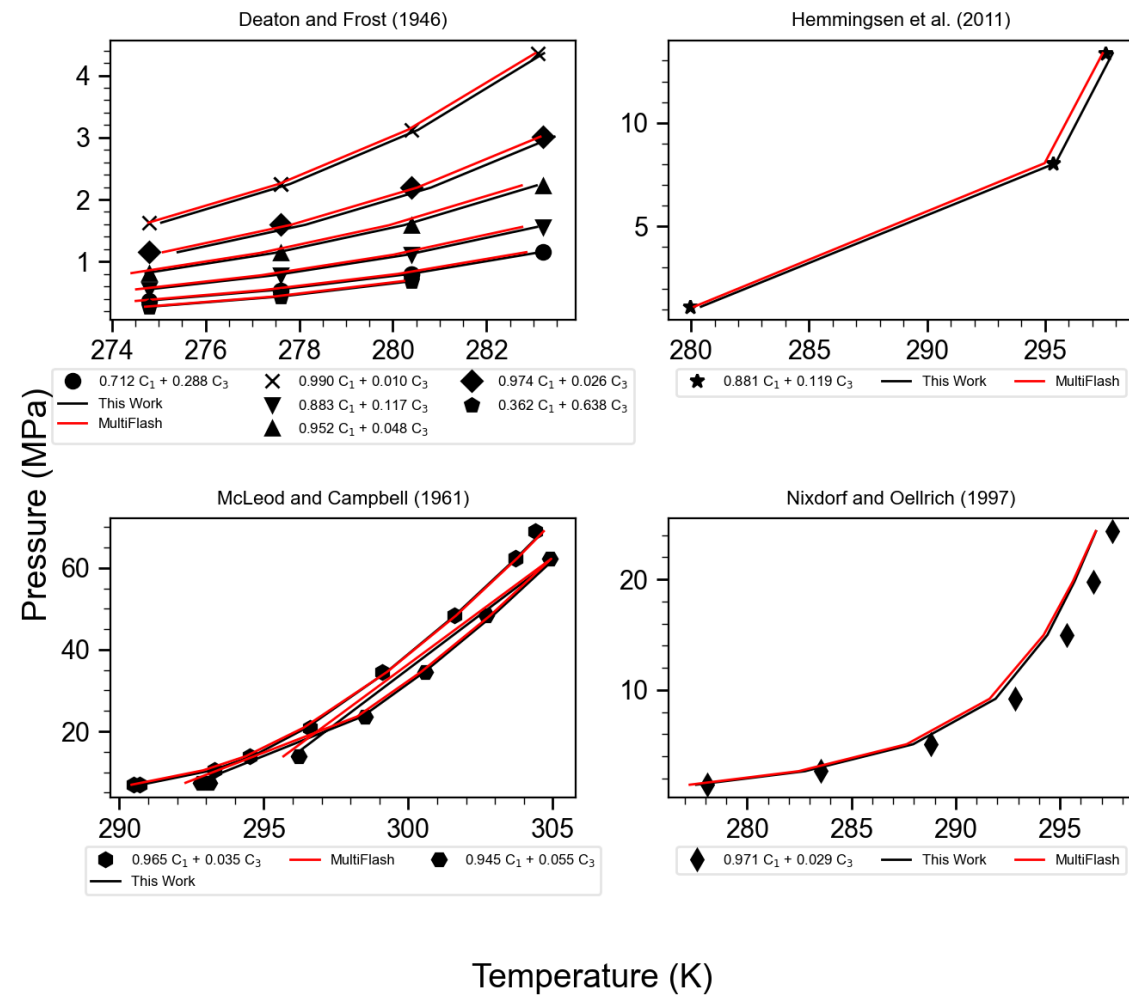


Figure S26: Selected hydrate equilibrium datasets for $\text{CH}_4 + \text{C}_3\text{H}_8$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{16,40,46,134}

3.2.2. CH₄ + C₂H₆ binary-gas mixture hydrate equilibria

Table S17: Database of CH₄ and C₂H₆ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AA DT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Bruusgaard et al. (2010) ¹³⁸	Lw-H-V	II	0.118	0.648	0.249	275.3	281.1	1.41	2.65	0.3030	0.8390	5	Te
	Lw-H-V	I	0.452	0.231	0.239	275.1	281.2	0.69	1.92	0.3030	0.8390	11	Te
Deaton and Frost (1946) ¹⁶	Lw-H-V	II	0.329	0.213	0.285	274.8	283.2	1.524	6.088	0.5640	0.1018	20	Tr
	Lw-H-V	I	0.027	0.303	0.393	274.8	283.2	0.945	2.434	0.5640	0.1018	4	Tr
Hashimoto et al. (2008) ⁷¹	Lw-H-V	I	0.339	0.186	0.170	279.1	288.1	1.12	12.3	0.1020	0.9910	21	Te
	Lw-H-V	II	0.358	0.795	0.411	279.1	288.1	1.89	11.9	0.1020	0.9910	34	Te
Holder and Grigoriou (1980) ⁷²	Lw-H-V	I	0.235	0.244	0.242	279.4	287.8	0.99	3.08	0.0160	0.1770	15	Tr
Hu et al. (2018) ¹³⁹	Lw-H-V	II	0.207	1.197	0.709	299.05	304.25	33.7	68	0.7470	0.7470	3	Te
Maekawa (2001) ³⁷	Lw-H-V	II	0.141	0.526	0.229	275.4	289.6	1.7	11.1	0.9020	0.1019	48	Te
	Lw-H-V	I	0.094	0.104	0.083	283.1	285.4	6.9	8.9	0.9020	0.1019	4	Te
McLeod and Campbell (1961) ⁴⁰	Lw-H-V	II	0.514	1.252	0.684	284.9	304.1	6.93	68.57	0.8090	0.9460	14	Tr
	Lw-H-V	I	0.611	1.041	0.089	301.2	302	62.23	68.43	0.8090	0.9460	2	Te
Nixdorf and Oelrich (1997) ⁴⁶	Lw-H-V	II	0.270	0.411	0.152	278.21	295.52	2.254	23.1101	0.9047	0.9047	8	Tr
Subramanian et al. (2000) ¹⁴⁰	Lw-H-V	II	0.581	0.057	0.817	274.2	274.2	0.1016	1.448	0.5810	0.9180	3	Te
	Lw-H-V	I	0.490	0.042	0.604	274.2	274.2	0.883	0.972	0.5810	0.9180	3	Tr
Training	—	—	0.329	0.470	0.367	274.2	304.1	0.883	68.57	0.0160	0.9460	64	—
Test	—	—	0.272	0.521	0.286	274.2	304.25	0.1016	68.43	0.1020	0.9910	131	—
Overall	—	—	0.289	0.504	0.313	334.2	304.25	0.69	68.57	0.0160	0.9910	195	—

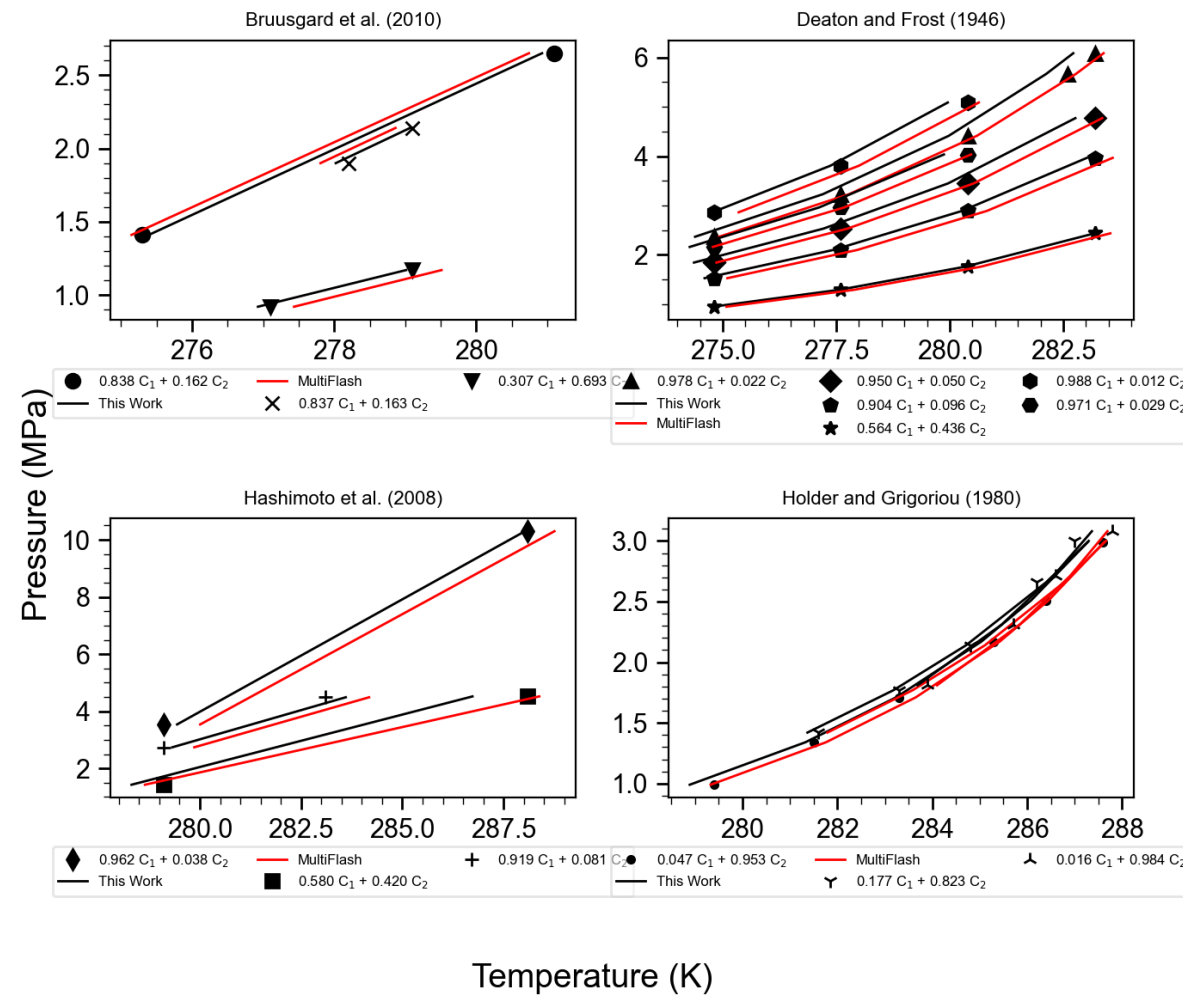


Figure S27: Selected hydrate equilibrium datasets $\text{CH}_4 + \text{C}_2\text{H}_6$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{16,71,72,141}

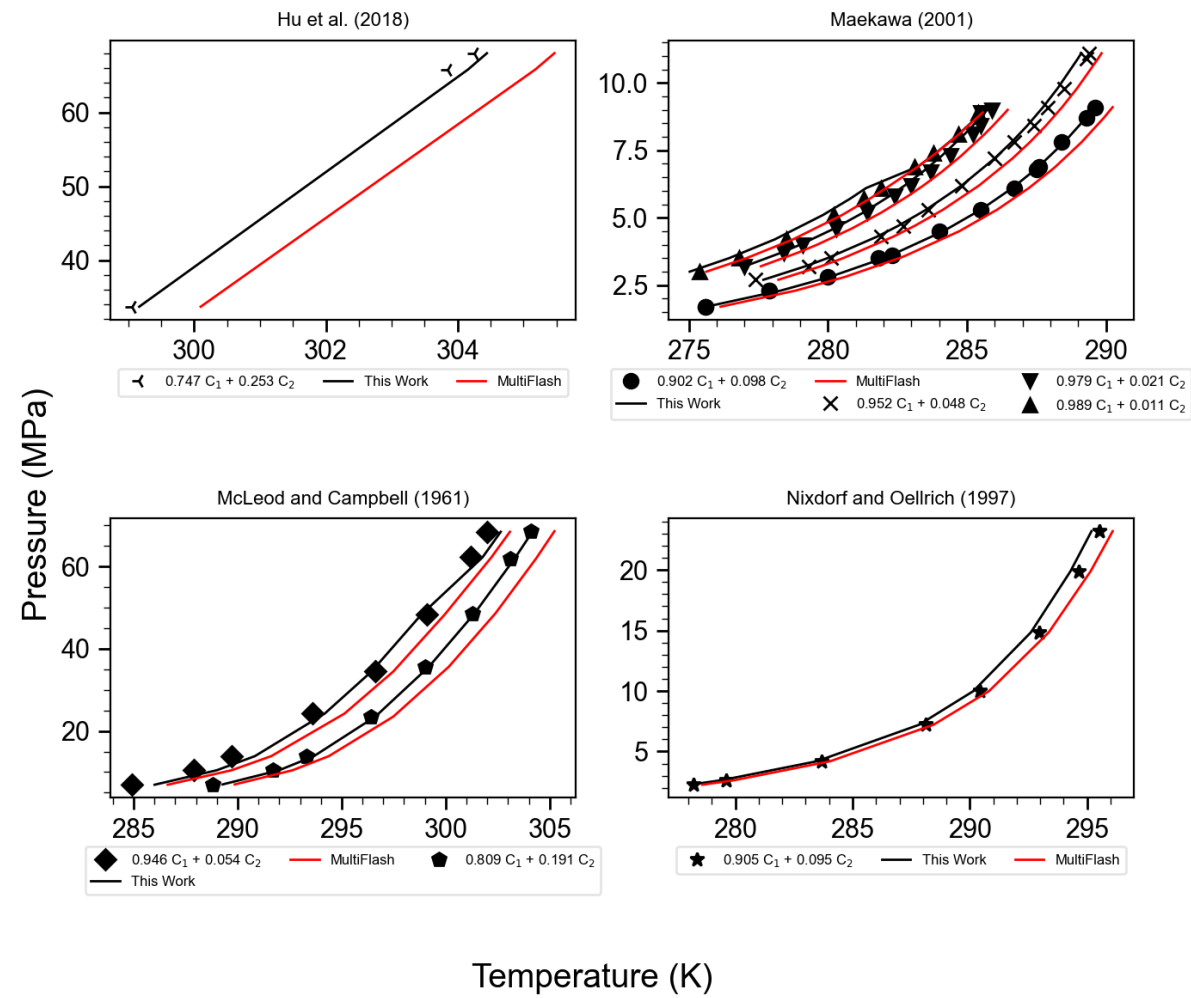


Figure S28: Selected hydrate equilibrium datasets $\text{CH}_4 + \text{C}_2\text{H}_6$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{37,40,46,139}

3.2.3. C₂H₆ + C₃H₈ binary-gas mixture hydrate equilibria

Table S18: Database of C₂H₆ + C₃H₈ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types:

'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Holder (1976) ¹⁴²	Lw-H-V	II	0.383	0.251	0.130	273.43	277.87	0.441	1.158	0.2800	0.8570	36	Te
	Lw-H-V	I	0.404	0.199	0.306	273.04	283.21	0.538	2.027	0.2800	0.8570	24	Te
Holder and Hand (1982) ⁷³	Lw-H-V-	I	0.450	0.205	0.336	273.4	285.3	0.49	2.03	0.1680	0.8570	25	Te
	LHC												
	Lw-H-V	I	0.698	0.437	0.550	273.1	284.5	0.54	7.28	0.1680	0.8570	11	Te
Jager (2001) ²⁷	Lw-H-V	II	0.397	0.302	0.118	273.9	278.6	0.44	2.79	0.1680	0.8570	37	Tr
	Lw-H-V	II	0.135	0.154	0.239	276.8	278.2	0.55	0.76	0.2964	0.2964	7	Te
Mooijer-van den Heuvel (2004) ¹⁴³	Lw-H-V	II	0.380	0.396	0.075	277.03	278.17	0.54	0.67	0.2990	0.2990	5	Tr
Nixdorf and Oellrich (1997) ⁴⁶	Lw-H-V	I	0.578	0.150	0.485	276.66	283.32	0.825	1.936	0.8515	0.8515	6	Te
Training	—	—	0.395	0.313	0.113	273.9	278.6	0.44	2.79	0.1680	0.8570	42	—
Test	—	—	0.430	0.236	0.285	273.04	285.3	0.441	7.28	0.1680	0.8570	109	—
Overall	—	—	0.420	0.257	0.237	273.04	285.3	0.44	7.28	0.1680	0.8570	151	—

3.2.4. CH₄ + CO₂ binary-gas mixture hydrate equilibria

Table S19: Database of CH₄ + CO₂ binary-gas mixture hydrate equilibrium datam with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AA DT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Adisasmito et al. (1991) ⁸	Lw-H-V	I	0.148	0.088	0.164	273.7	287.6	1.45	10.95	0.1500	0.9200	42	Tr
Belandria et al. (2010) ¹⁴⁴	Lw-H-V	I	0.561	0.631	0.548	279.1	289.9	2.96	13.06	0.2700	0.7360	11	Te
Belandria et al. (2011a) ¹⁴⁵	Lw-H-V	I	0.346	0.238	0.360	273.6	285.5	1.51	8.27	0.0570	0.7940	49	Te
Belosludov et al. (2018) ¹⁴⁶	Lw-H-V	I	3.012	2.942	2.294	273	277	1.06	3.09	0.3000	0.7000	6	Te
Beltran and Servio (2008) ¹⁴⁷	Lw-H-V	I	1.122	1.260	1.025	275.14	285.34	1.92	7.47	0.5450	0.8690	23	Te
Bruusgaard et al. (2010) ¹³⁸	Lw-H-V	I	0.040	0.093	0.197	274.02	280.12	1.66	4.03	0.3320	0.7970	12	Tr
Chapoy et al. (2015) ¹⁴⁸	Lw-H-V	I	0.455	0.375	0.308	276	286.95	1.82	19.97	0.0590	0.0590	7	Te
Fan and Guo (1999) ⁸⁷	Lw-H-V	I	0.842	0.759	0.760	273.5	282.3	1.1	4.8	0.0348	0.0348	9	Tr
Fan et al. (2019) ¹⁴⁹	Lw-H-V	I	0.249	0.236	0.233	278.68	286.46	4.33	10.06	0.9200	0.9200	5	Tr
Hachikubo et al. (2002) ²³	Lw-H-V	I	1.162	1.027	1.493	271.25	271.41	1.271	2.022	0.2300	0.7500	3	Te
Herri et al. (2011) ¹⁵⁰	Lw-H-V	I	0.223	0.108	0.367	277.15	277.15	2.36	3.55	0.3600	0.8900	4	Tr
Kastanidis et al. (2017) ¹⁵¹	Lw-H-V	I	1.284	1.163	1.369	274.3	289.2	2.63	12.55	0.7190	0.7506	15	Te
Khan et al. (2019) ¹⁵²	Lw-H-V	I	0.129	0.152	0.078	275.2	285	1.98	6.52	0.5000	0.5000	4	Tr
Le Quang et al. (2016) ¹⁵³	Lw-H-V	I	0.181	0.115	0.245	275.35	282.65	2.91	5.63	0.7750	0.8800	14	Tr
Lee et al. (2012) ⁹⁴	Lw-H-V	I	0.107	0.101	0.235	274	278	1.53	3.65	0.1920	0.8910	12	Tr
Legoix et al. (2018) ¹⁵⁴	Lw-H-V	I	0.345	0.358	0.133	280.92	284.97	3.41	6.206	0.1004	0.1004	3	Tr
Mu et al. (2018) ⁴³	Lw-H-V	I	0.068	0.122	0.005	279.9	286.37	3.381	7.935	0.4974	0.4974	6	Tr
Obanijesu et al. (2014) ¹⁵⁵	Lw-H-V	I	5.085	5.011	4.946	282.95	286.65	10	20	0.7800	0.7800	5	Te
Ohgaki et al. (1996) ⁴⁷	Lw-H-V	I	0.076	0.193	0.038	280.3	280.3	3.24	4.99	0.3170	0.9350	29	Te
Partoon et al. (2016) ¹⁵⁶	Lw-H-V	I	0.644	0.763	0.689	281.35	284.65	3.25	5.32	0.2990	0.2990	3	Tr
Sabil et al. (2014) ⁵²	Lw-H-V	I	0.747	0.800	0.757	280.35	287.95	2.76	11.28	0.2751	0.2751	5	Te
Sadeq et al. (2017) ⁵³	Lw-H-V	I	0.343	0.379	0.364	280.55	293.95	5	25	0.8000	0.9000	18	Te
Seo et al. (2000) ¹⁰⁶	Lw-H-V	I	0.363	0.357	0.253	272.66	283.56	1.5	5	0.0959	0.8146	19	Tr
Servio et al. (1999) ¹⁵⁷	Lw-H-V	I	0.374	0.387	0.416	273.5	283.1	1.78	5.07	0.4653	0.8756	17	Tr
Shi et al. (2014) ¹⁵⁸	Lw-H-V	I	0.253	0.160	0.212	280.9	286.8	4.07	8.55	0.5000	0.5000	6	Tr
Sun et al. (2016) ¹⁰⁸	Lw-H-V	I	0.043	0.064	0.053	276.15	278.15	1.772	2.288	0.0490	0.0505	9	Tr
Unruh and Katz (1949) ¹¹⁰	Lw-H-V	I	0.292	0.345	0.326	275.5	285.7	1.99	7	0.2900	0.9450	17	Tr
Zang and Liang (2017) ¹⁵⁹	Lw-H-V	I	0.197	0.328	0.146	278.2	284.1	2.76	5.61	0.5000	0.5000	5	Tr

Reference	Phases	Structure	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	$x_{1,min}$	$x_{1,max}$	N	Type
Zhang et al. (2016) ¹⁶⁰	Lw-H-V	I	0.109	0.078	0.272	273.7	276.4	1.45	3.1	0.2100	0.9100	6	Tr
Training	—	—	0.238	0.226	0.256	272.66	287.6	1.1	10.95	0.0348	0.9450	193	—
Test	—	—	0.763	0.760	0.727	271.25	293.95	1.06	25	0.0570	0.9350	171	—
Overall	—	—	0.556	0.477	0.477	271.25	293.95	1.06	25	0.0355	0.9450	364	—

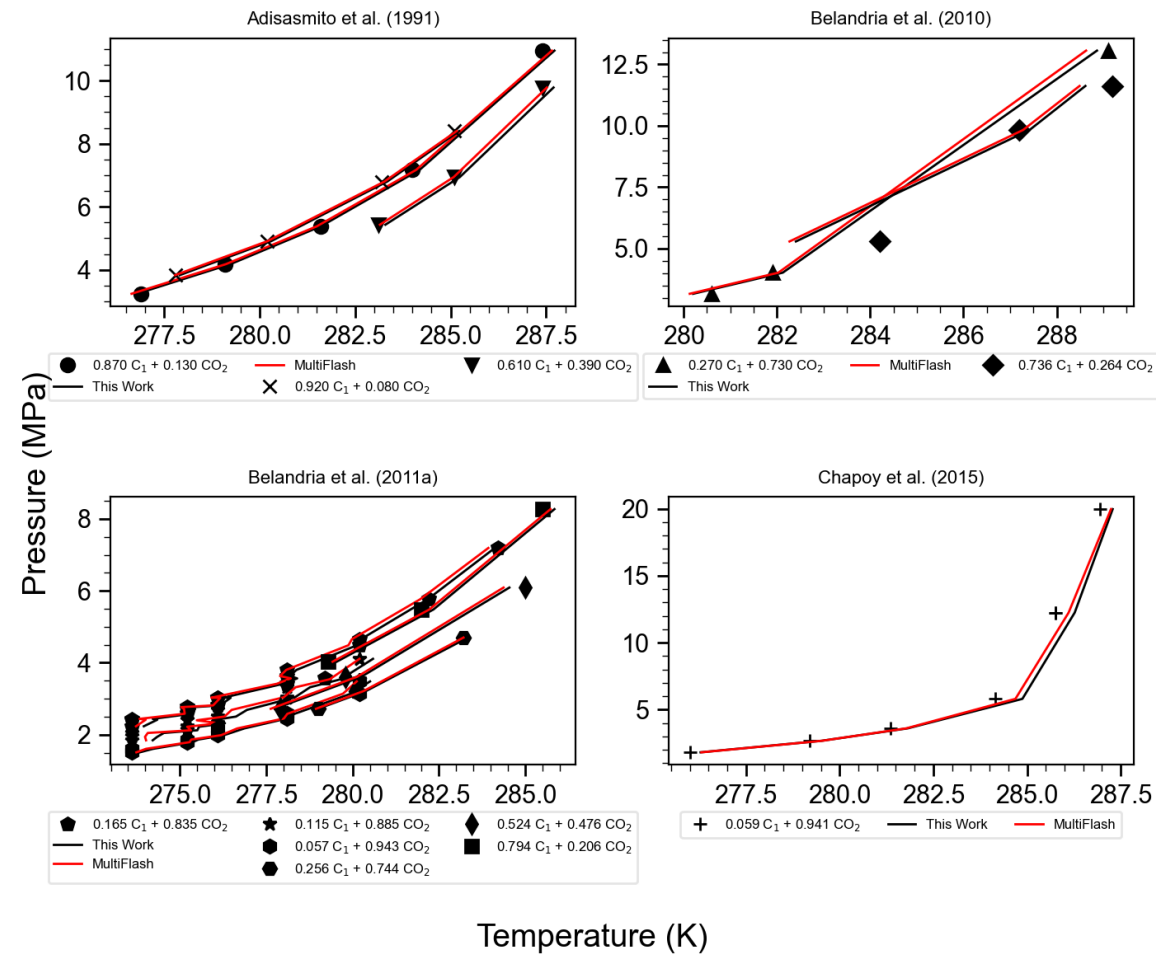


Figure S30: Selected hydrate equilibrium datasets $\text{CH}_4 + \text{CO}_2$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{8,144,145,148}

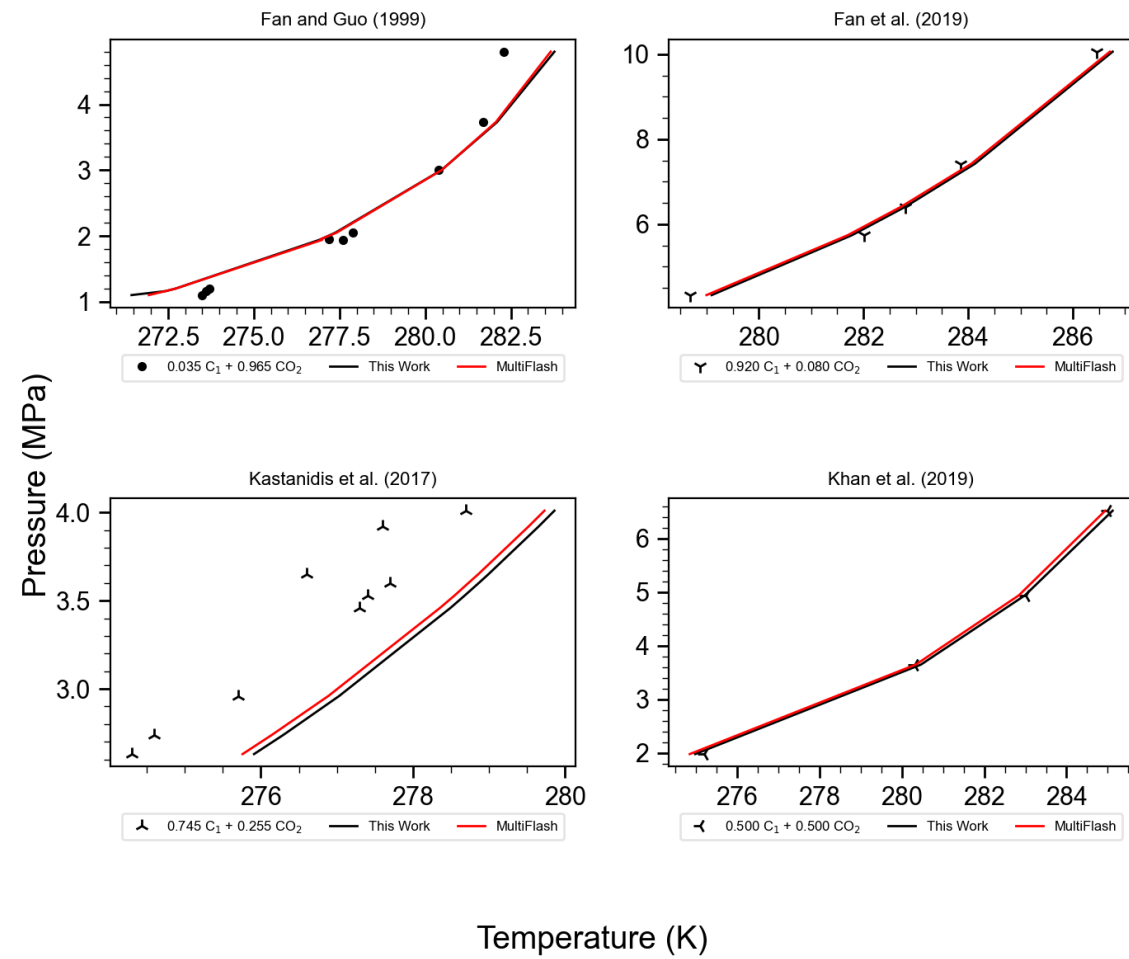


Figure S31: Selected hydrate equilibrium datasets CH₄ + CO₂ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{87,149,151,152}

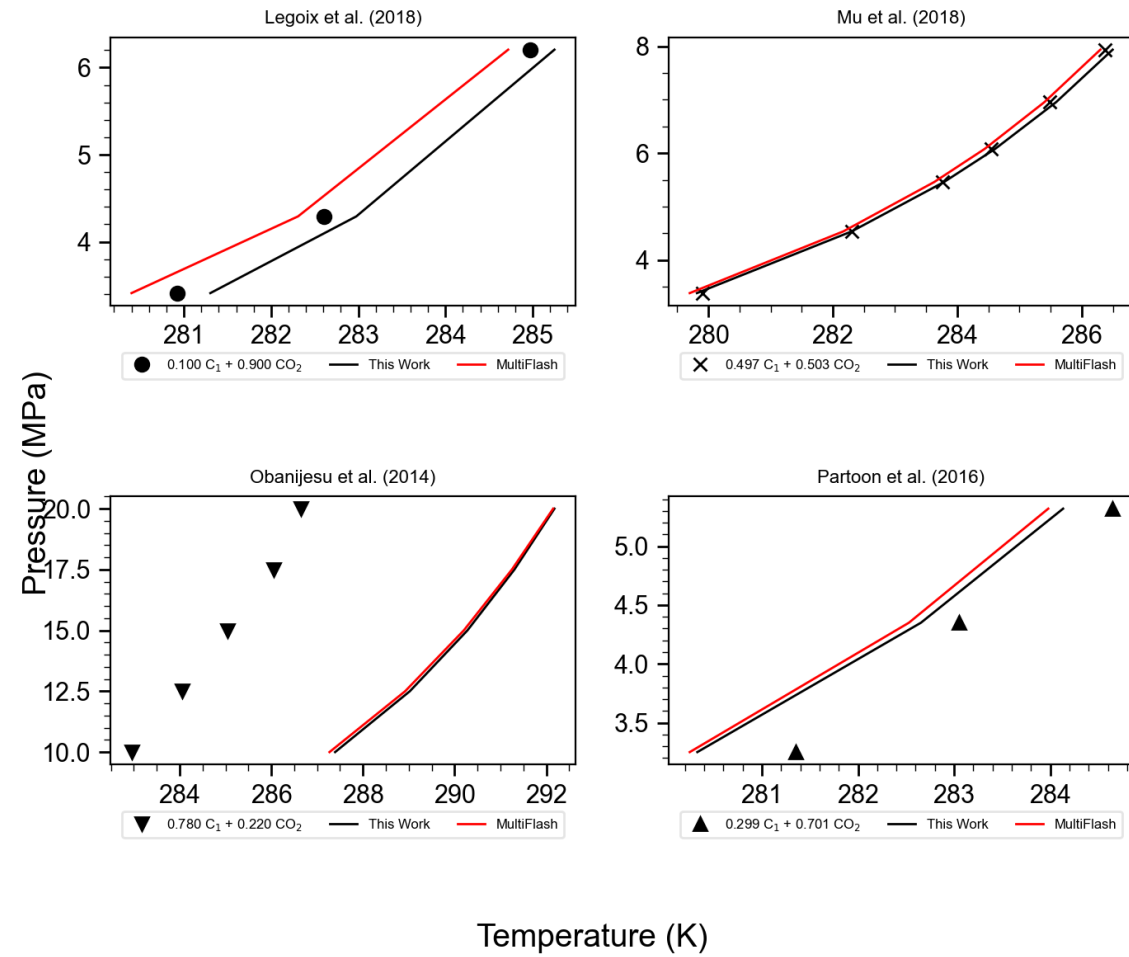


Figure S32: Selected hydrate equilibrium datasets CH₄ + CO₂ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{43,154–156}

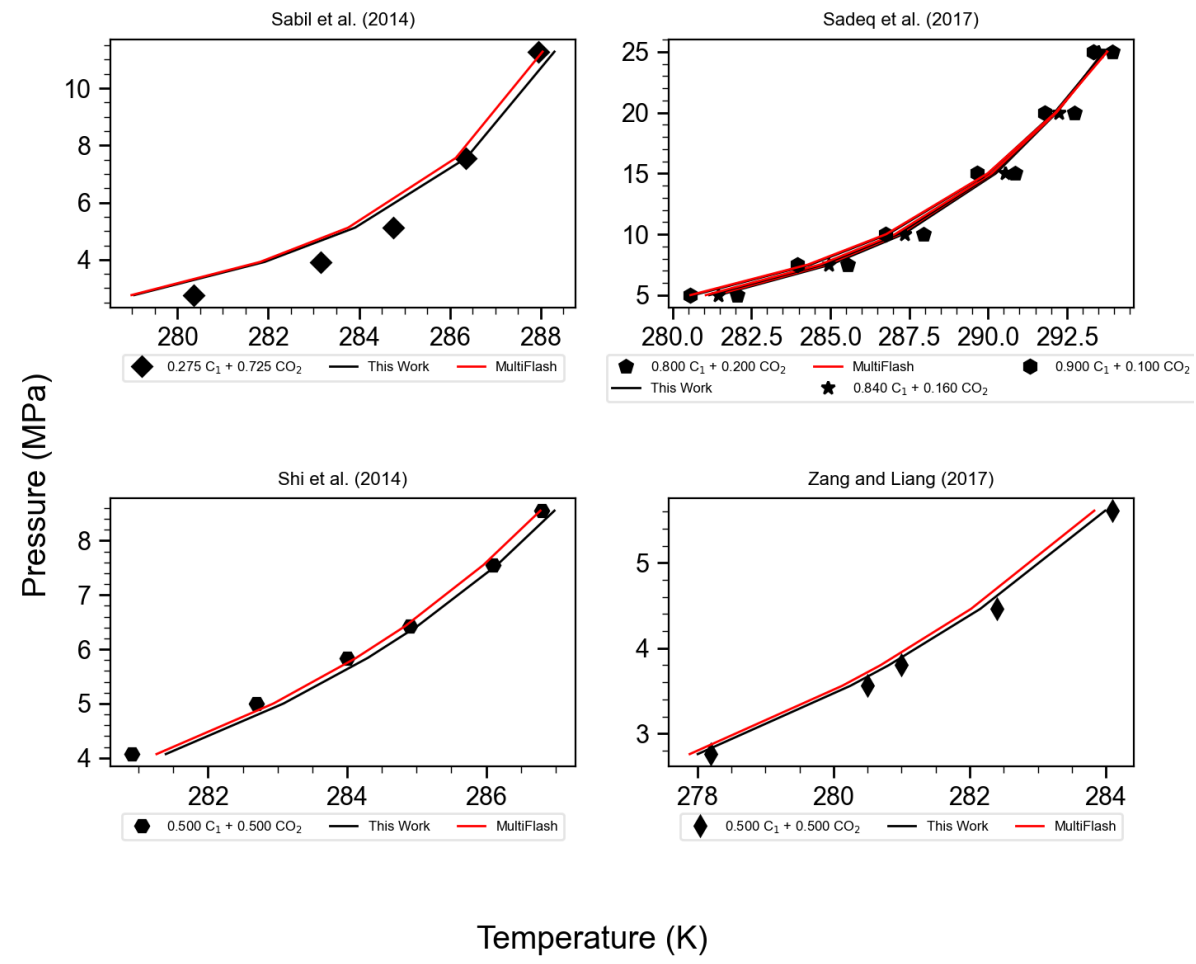


Figure S33: Selected hydrate equilibrium datasets $\text{CH}_4 + \text{CO}_2$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{52,53,158,159}

3.2.5. C₂H₆ + CO₂ binary-gas mixture hydrate equilibria

Table S20: Database of C₂H₆ + CO₂ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types:

'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AA DT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Adisasmito and Sloan (1992) ¹⁶¹	Lw-H- V	I	0.213	0.406	0.409	273.5	287.8	0.5654	4.0817	0.0330	0.8110	40	Te
Fan and Guo (1999) ⁸⁷	Lw-H- V	I	0.456	0.571	0.109	276	282.7	1.58	3.9	0.0531	0.0531	5	Te
Matsui et al. (2010) ⁷⁶	Lw-H- V	I	0.284	0.652	0.100	274.15	284.15	0.545	5.68	0.0210	0.9560	54	Te
Overall/Test	—	—	0.264	0.549	0.145	273.5	287.8	0.545	5.68	0.0210	0.9560	99	—

3.2.6. C₃H₈ + CO₂ binary-gas mixture hydrate equilibria

Table S21: Database of C₃H₈ + CO₂ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types:

'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AA DT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Robinson and Mehta (1971) ¹⁰²	Lw-H- V	II	0.598	0.410	0.713	273.8167	286.15	0.30	4.27	0.0550	0.8600	37	Te
Adisasmito and Sloan (1992) ¹⁶¹	Lw-H- V	II	0.489	0.660	1.262	273.7	282	0.22	3.80	0.0100	0.9010	41	Tr

Reference	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	$x_{1,min}$	$x_{1,max}$	N	Type
Adisasmito and Sloan (1992) ¹⁶¹	Lw-H- V	I	0.447	0.194	1.505	273.7	282	1.36	3.82	0.0100	0.9010	14	Te
Ng and Robinson (1976) ¹⁶²	Lw-H- V	II	0.536	0.366	0.594	273.9278	281.8167	0.30	1.30	0.0600	0.8400	13	Tr
Training	—	—	0.500	0.589	1.101	273.7	282	0.22	3.80	0.0100	0.9010	54	—
Test	—	—	0.557	0.351	0.931	273.7	286.15	0.30	4.27	0.0100	0.9010	51	—
Overall	—	—	0.528	0.473	1.018	273.7	286.15	0.22	4.27	0.0100	0.9010	105	—

3.2.1. CH₄ + N₂ binary-gas mixture hydrate equilibria

Table S22: Database of CH₄ + N₂ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	$x_{1,min}$	$x_{1,max}$	N	Type
Jhaveri and Robinson (1965) ³⁰	Lw-H-V	I	0.764	0.975	1.102	273.2	295.2	3.9	35.96	0.1270	0.8920	44	Te
Lee et al. (2006) ¹⁶³	Lw-H-V	I	0.684	0.873	0.931	273.3	285.05	7.1	20.7	0.5961	0.7476	16	Tr
Lee et al. (2006) ¹⁶³	Lw-H-V	II	1.282	0.713	0.675	273.3	281	8.625	17.45	0.5961	0.7476	4	Te
Mei et al. (1996) ¹⁶⁴	Lw-H-V	I	0.141	0.153	0.133	273.7	285.3	2.99	10.1	0.1074	0.1074	8	Tr
Nixdorf and Oellrich (1997) ⁴⁶	Lw-H-V	I	0.109	0.160	0.206	278.7	292.44	4.938	24.428	0.1074	0.1074	6	Tr
Sadeq et al. (2017) ⁵³	Lw-H-V	I	0.485	0.589	0.632	276.75	292.75	5	25	0.1000	0.3600	23	Tr
Training	—	—	0.451	0.560	0.599	273.3	292.75	2.99	25.00	0.1000	0.7476	53	—
Test	—	—	0.807	0.953	1.067	273.2	295.2	3.90	35.96	0.1270	0.8920	48	—
Overall	—	—	0.620	0.747	0.821	273.2	295.2	2.99	35.96	0.1000	0.8920	101	—

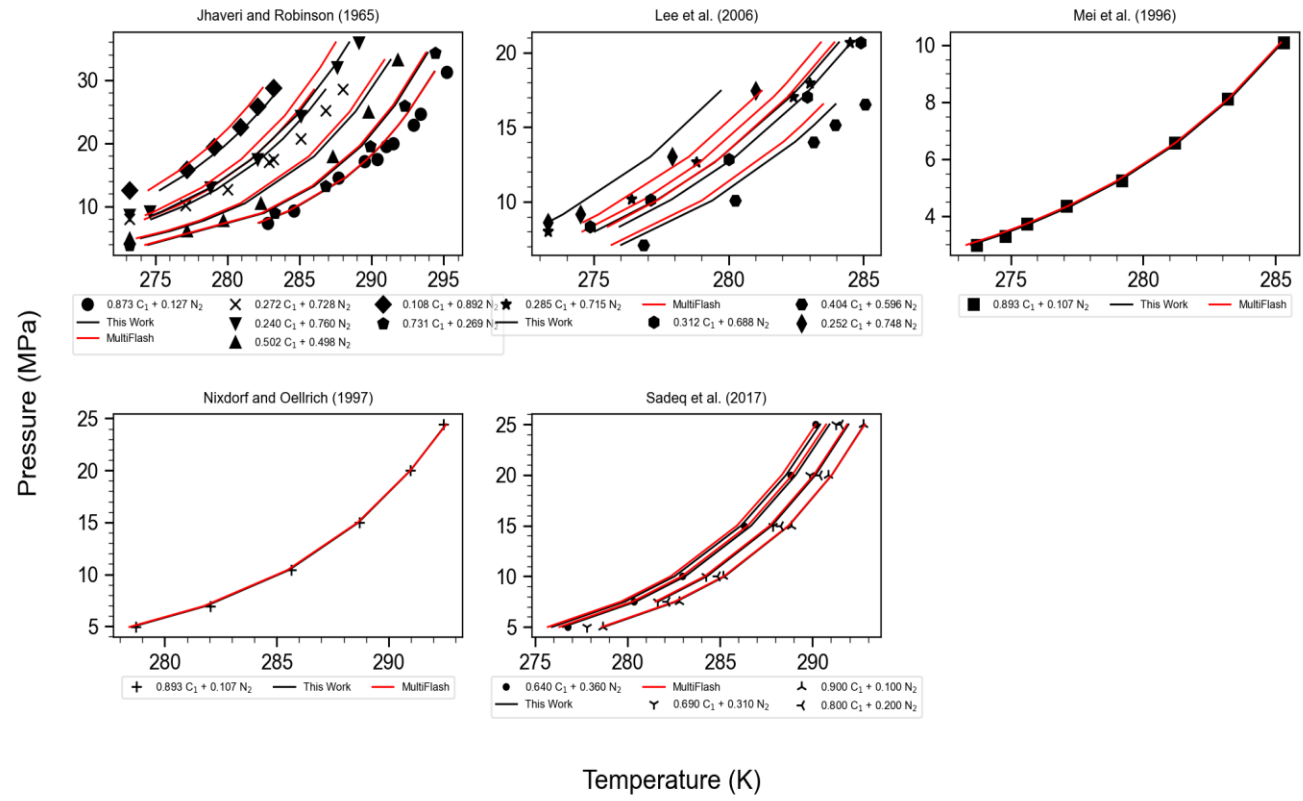


Figure S34: Selected hydrate equilibrium datasets $\text{CH}_4 + \text{N}_2$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{30,46,53,163,164}

3.2.2. $C_3H_8 + N_2$ binary-gas mixture hydrate equilibria

Table S23: Database of $C_3H_8 + N_2$ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	$x_{1,min}$	$x_{1,max}$	N	Type
Ng et al. (1977) ¹⁶⁵	Lw-H-LHC-V	II	0.351	0.118	0.226	278.98	293.8	0.76	16.99	0.0100	0.9906	16	Te
	Lw-H-LHC	II	0.302	0.104	0.301	280.13	291.3	1.98	15.31	0.0100	0.9906	21	Te
	Lw-H-V	II	0.394	0.334	0.469	274.16	289.17	0.256	18.09	0.0100	0.9906	29	Tr
Training	—	—	0.394	0.334	0.469	274.16	289.17	0.26	18.09	0.0100	0.9906	29	—
Test	—	—	0.323	0.110	0.269	278.98	293.8	0.76	16.99	0.0100	0.9906	37	—
Overall	—	—	0.354	0.208	0.357	274.16	293.8	0.256	18.09	0.0100	0.9906	66	—

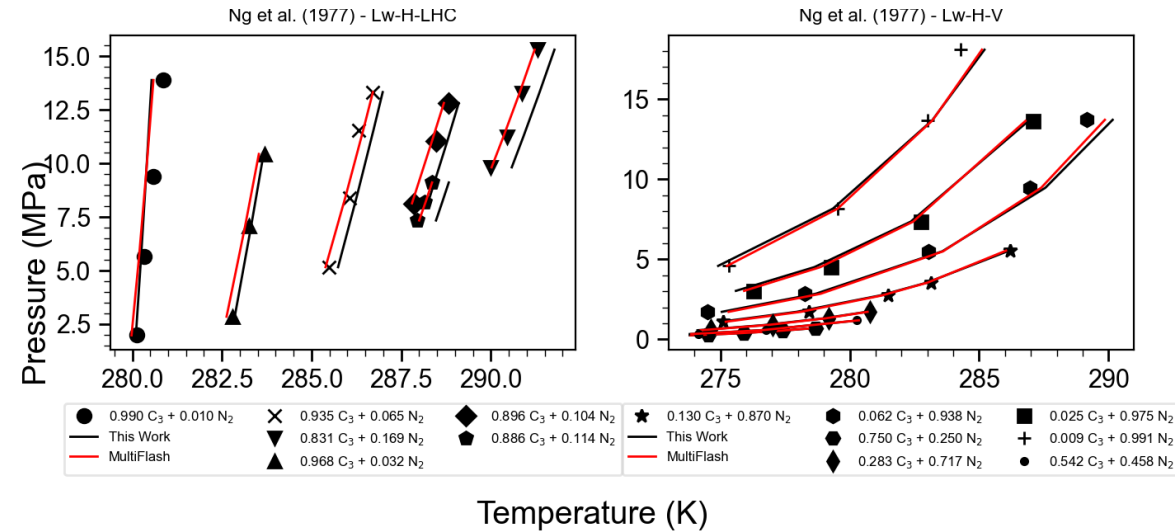


Figure S35: Selected hydrate equilibrium datasets $C_3H_8 + N_2$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:¹⁶⁵

3.2.3. N₂ + CO₂ binary-gas mixture hydrate equilibria

Table S24: Database of N₂ + CO₂ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Belandria et al. (2011) ¹⁶⁶	Lw-H-V	I	2.380	1.874	1.912	273.6	281.7	2.032	17.628	0.0695	0.5842	35	Te
Belandria et al. (2012) ¹⁶⁷	Lw-H-V	I	1.598	1.208	1.208	275.1	278.9	2.35	16.74	0.2510	0.8490	14	Te
Bruusgaard et al. (2008) ¹⁴¹	Lw-H-V	I	0.221	0.287	0.243	275.2	283.1	2	22.4	0.2130	0.8380	24	Te
Chapoy et al. (2015) ¹⁴⁸	Lw-H-V	I	0.191	0.202	0.128	276.91	288.55	2.05	55.11	0.0460	0.0460	6	Te
Fan and Guo (1999) ⁸⁷	Lw-H-V	I	0.367	0.371	0.313	273.1	280.2	1.22	3.09	0.0348	0.0901	9	Te
Herri et al. (2011) ¹⁵⁰	Lw-H-V	I	0.691	2.809	0.862	273.4	281.1	5.3	6.6	0.4200	0.8400	16	Te
Jarrahian and Nakhaee (2019) ⁹¹	Lw-H-V	I	1.919	1.083	1.086	274.15	280.15	5.87	29.01	0.7500	0.9500	35	Te
Kang et al. (2001) ¹⁶⁸	Lw-H-V	I	0.933	0.725	0.866	272.85	284.25	1.565	20.753	0.0341	0.9502	35	Te
Kang et al. (2001) ¹⁶⁸	Lw-H-V	II	2.938	1.902	1.838	273.95	280	11.02	26.69	0.0341	0.9502	13	Tr
Kim et al. (2011) ¹⁶⁹	Lw-H-V	I	1.978	0.444	0.402	276.88	285.41	5	20	0.0027	0.0540	16	Te
Kim et al. (2011) ¹⁶⁹	Lw-H-V-LHC	I	0.489	0.226	0.076	283.33	284.29	5.5	10	0.0027	0.0540	17	Te
Lee et al. (2014) ¹²⁰	Lw-H-V	I	1.476	1.639	0.591	275	281.1	8.23	24.51	0.8000	0.9000	17	Te
Olsen et al. (1999) ¹⁷⁰	Lw-H-V	I	0.273	0.184	0.142	273.4	281.9	1.986	9.55	0.2811	0.8380	15	Te
Rho et al. (2018) ¹⁷¹	Lw-H-V	I	0.384	0.377	0.149	277.82	280.52	2.5	3.5	0.0229	0.0229	3	Te
Sadeq et al. (2017) ⁵³	Lw-H-V	I	0.608	0.757	0.695	275.75	284.45	5	20	0.6400	0.7400	10	Te
Sun et al. (2015) ¹⁷²	Lw-H-V	I	2.375	1.711	1.783	273.4	278.4	5.28	17.53	0.7490	0.8990	17	Te
Training	—	—	2.938	1.902	1.838	273.95	280	11.02	26.69	0.0341	0.9502	13	—
Test	—	—	1.275	1.047	0.866	272.85	288.55	1.22	55.11	0.0027	0.9502	269	—
Overall	—	—	1.368	1.086	0.911	272.85	288.55	1.22	55.11	0.0027	0.9502	282	—

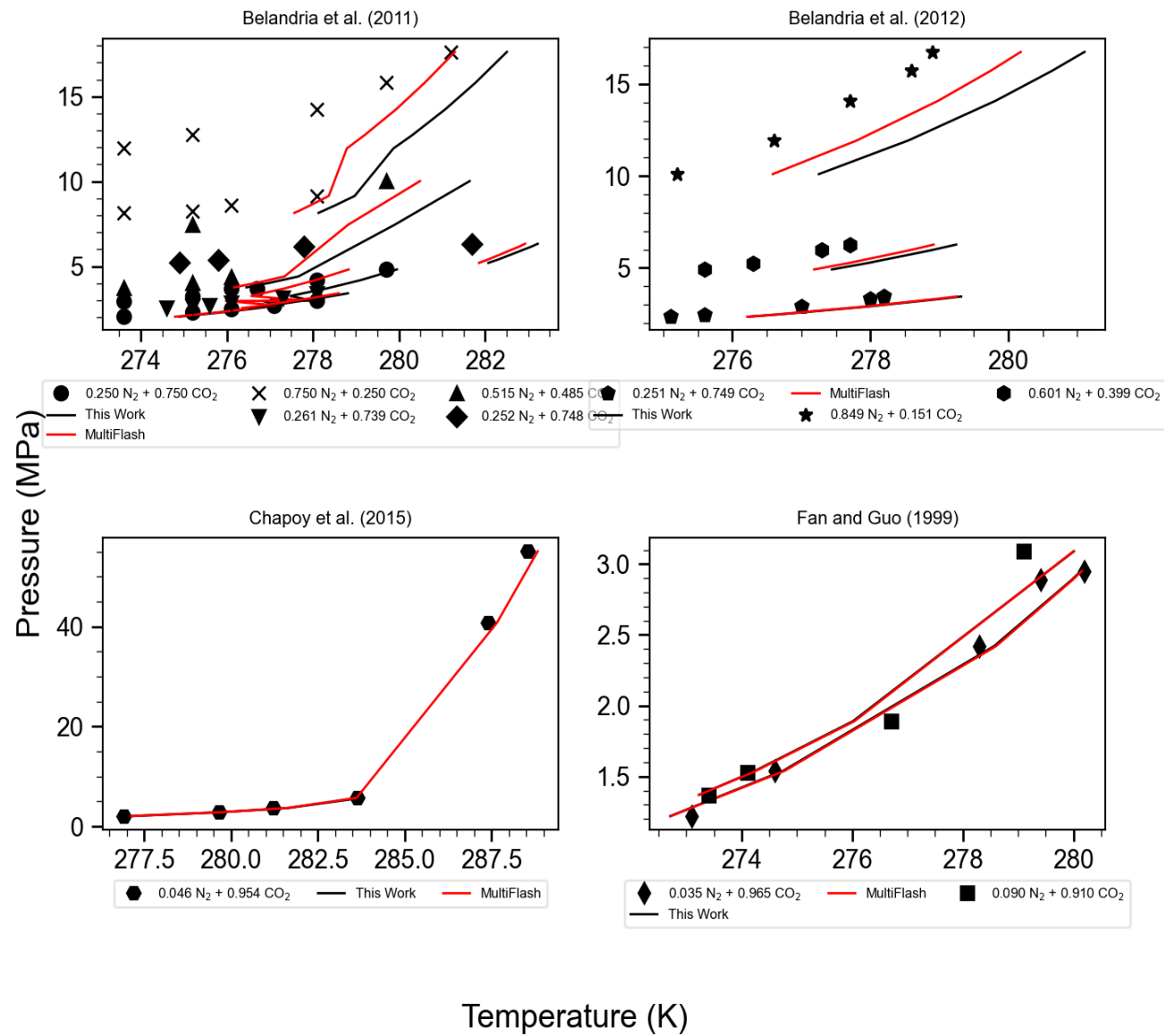


Figure S36: Selected hydrate equilibrium datasets $N_2 + CO_2$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{87,148,166,167}. Note for Belandria et al. (2011)¹⁶⁶ and Bellandria et al.¹⁶⁷, the composition of $N_2 + CO_2$ is normalised against itself (the gas-phase); the reader should refer to the source for the original composition.

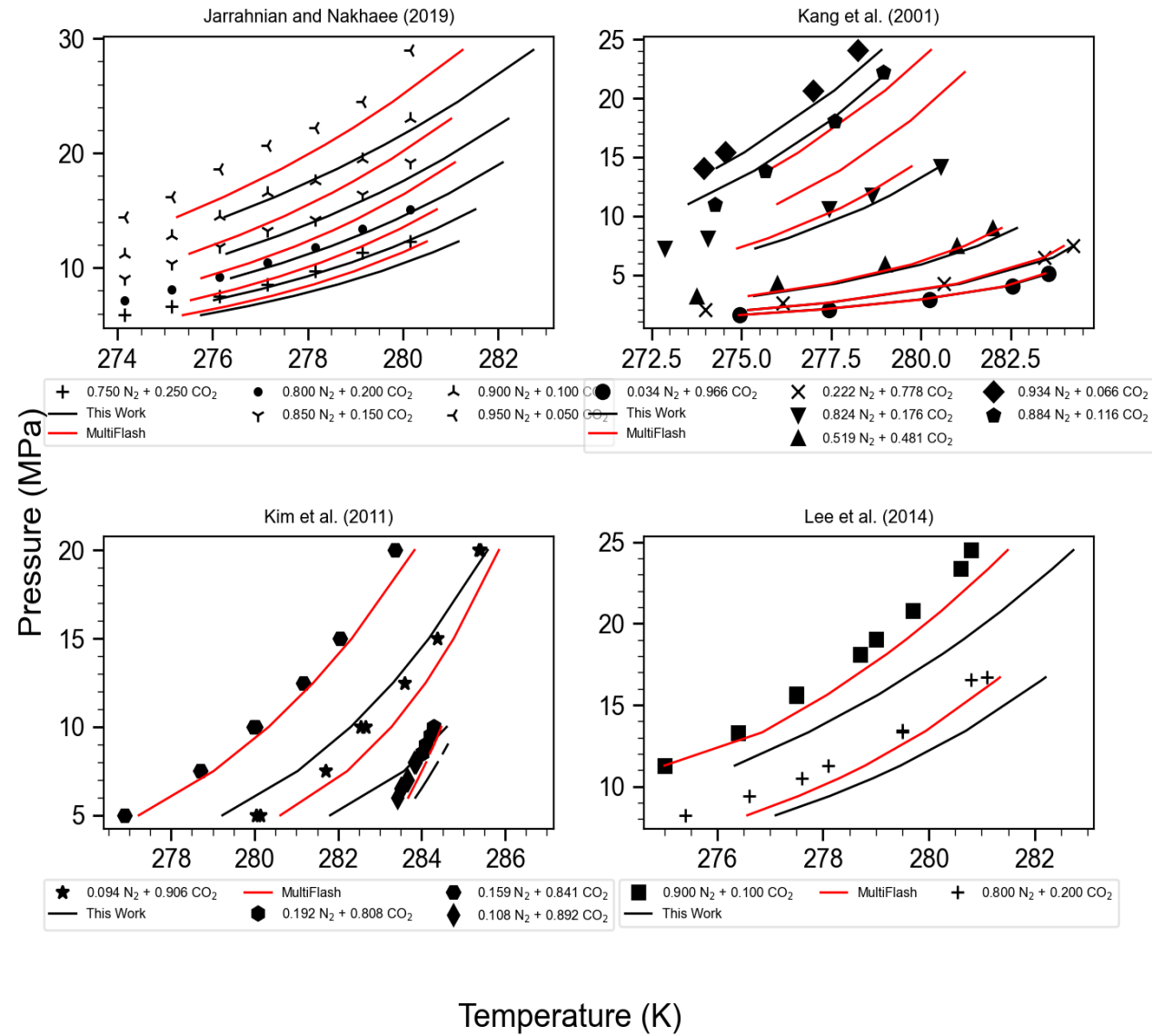


Figure S37: Selected hydrate equilibrium datasets $N_2 + CO_2$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{91,120,168,169}. Note for Kim et al. (2011)¹⁶⁹ the composition of $N_2 + CO_2$ is normalised against itself (the gas-phase); the reader should refer to the source for the original composition.

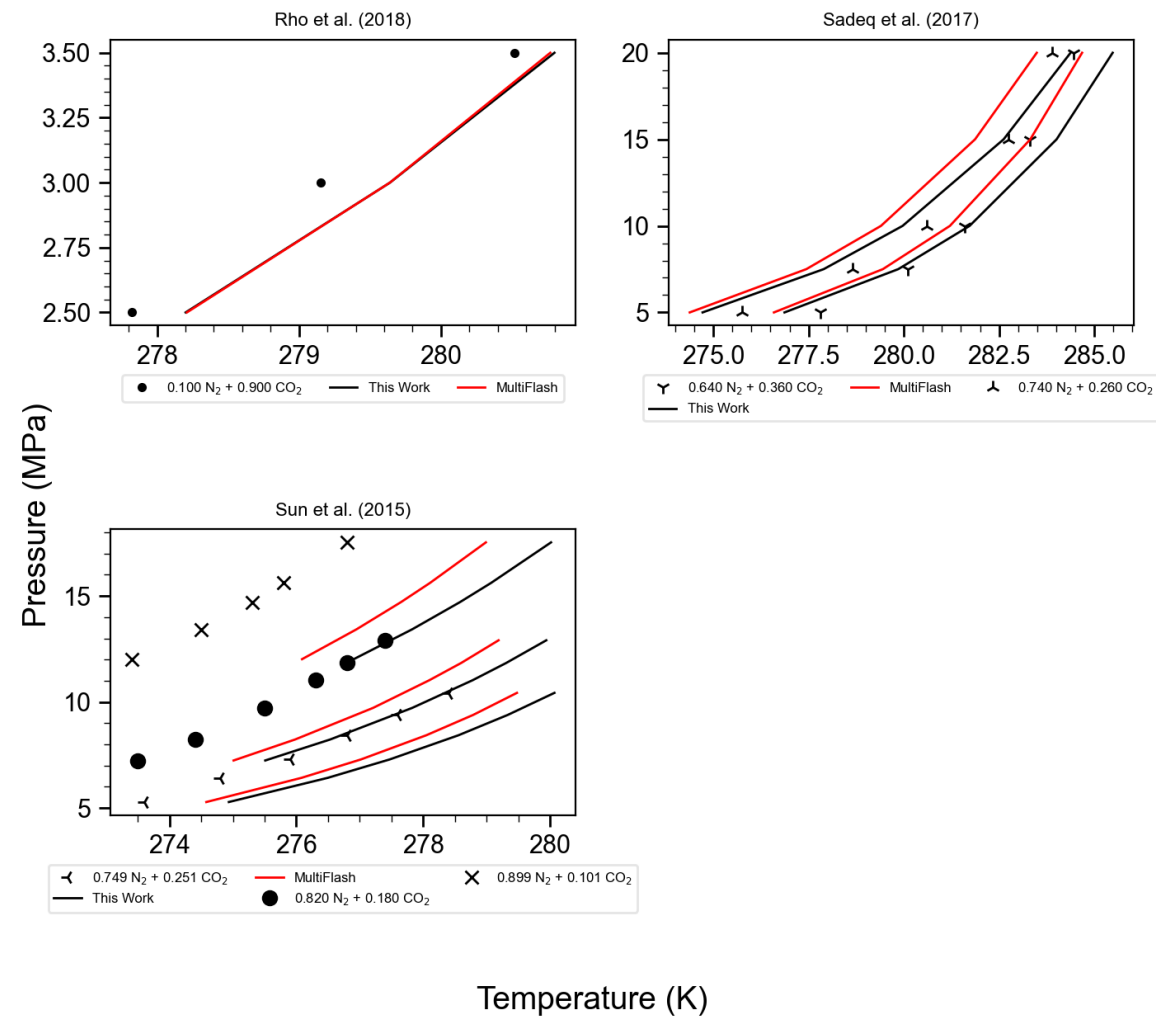


Figure S38: Selected hydrate equilibrium datasets $N_2 + CO_2$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{53,171,172}

3.2.4. CH₄ + H₂S binary-gas mixture hydrate equilibria

Table S25: Database of CH₄ + H₂S binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Noaker and Katz (1954) ¹⁷³	Lw-H- V	I	0.614	0.674	0.763	276.5	295.4	1.03	6.79	0.7800	0.9900	20	Tr
Mohammadi and Richon (2015) ¹⁷⁴	Lw-H- V	I	0.825	1.025	1.399	273.9	279.6	0.92	1.94	0.8960	0.9560	5	Te
Ward et al. (2015a) ¹⁷⁵	Lw-H- V	I	0.202	0.218	0.206	283.31	293.22	2	6.87	0.8833	0.8985	6	Te
Training	—	—	0.614	0.674	0.763	276.5	295.4	1.03	6.79	0.7800	0.9900	20	—
Test	—	—	0.486	0.585	0.748	273.9	293.22	0.92	6.87	0.8833	0.9560	11	—
Overall	—	—	0.569	0.642	0.758	273.9	295.4	0.92	6.87	0.7800	0.9900	31	—

3.2.5. CH₄ + n-C₄H₁₀ binary-gas mixture hydrate equilibria

Table S26: Database of CH₄ + n-C₄H₁₀ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types: 'Tr' = Training data; 'Te' = Test data. In the Phases column, the * denotes that no compositional data was available for these points, and an equimolar gas composition was assumed.

Reference	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Ng and Robinson (1976a) ¹⁷⁶	Lw-H-V	II	0.765	0.448	0.235	276	287.55	2.05	11.05	0.9418	0.9836	16	Tr
	Lw-H-V	I	0.168	0.173	0.063	287.4	288.5	12.06	13.72	0.9418	0.9836	2	Te
Ng and Robinson (1977) ¹⁶⁵	Lw-H-V-LHC	II	0.690	0.280	0.111	275	287.4	1.24	8.83	0.0870	0.5010	5	Tr
	Lw-H-LHC	II	0.654	1.081	1.013	275.6	288.5	2.96	13.82	0.0870	0.5010	24	Tr
Deaton and Frost (1946) ¹⁶	Lw-H-V	II	0.286	0.285	0.567	274.8	280.4	2.048	4.075	0.9740	0.9920	6	Te
McLeod and Campbell (1961) ⁴⁰	Lw-H-V	II	0.138	0.521	0.198	282.5	290.3	5.76	17.96	0.9470	0.9740	11	Te
	Lw-H-V	I	0.169	0.411	0.140	292.4	301.1	23.89	68.43	0.9470	0.9740	7	Te
John and Holder (1982a) ¹⁷⁷	I-H-V	II	0.937	1.555	1.020	251.2	273.1	0.391	2.611	0.5000	0.9960	44	Tr
	I-H-V-LHC	II	0.870	1.780	0.673	251.2	273.1	0.336	1.011	0.5000	0.9960	5	Tr
	I-H-V-LHC*	II	0.367	1.090	0.810	255.3	272.5	0.4171	0.979	0.5000	0.9960	19	Te
	Lw-H-V-LHC*	II	0.300	0.073	0.541	273.3	276.8	1.046	1.722	0.5000	0.9960	6	Te
Paranjpe et al. (1987) ¹³⁶	Lw-H-V-LHC	II	1.998	1.847	1.366	268.2	281.2	0.784	3.441	0.8900	0.9850	3	Te
Smith et al. (2017) ¹³⁷	Lw-H-V	II	0.420	0.446	0.440	275.35	288.05	2.75	12.53	0.9450	0.9948	12	Te
	Lw-H-V	I	0.283	0.263	0.264	281.65	290.55	6.26	16.01	0.9450	0.9948	6	Te
Training	—	—	0.819	1.190	0.818	251.2	288.5	0.34	13.82	0.0870	0.9960	94	—
Test	—	—	0.365	0.615	0.504	255.3	301.1	0.42	68.43	0.5000	0.9960	72	—
Overall	—	—	0.622	0.940	0.849	251.2	301.1	0.336	68.43	0.0870	0.9960	166	—

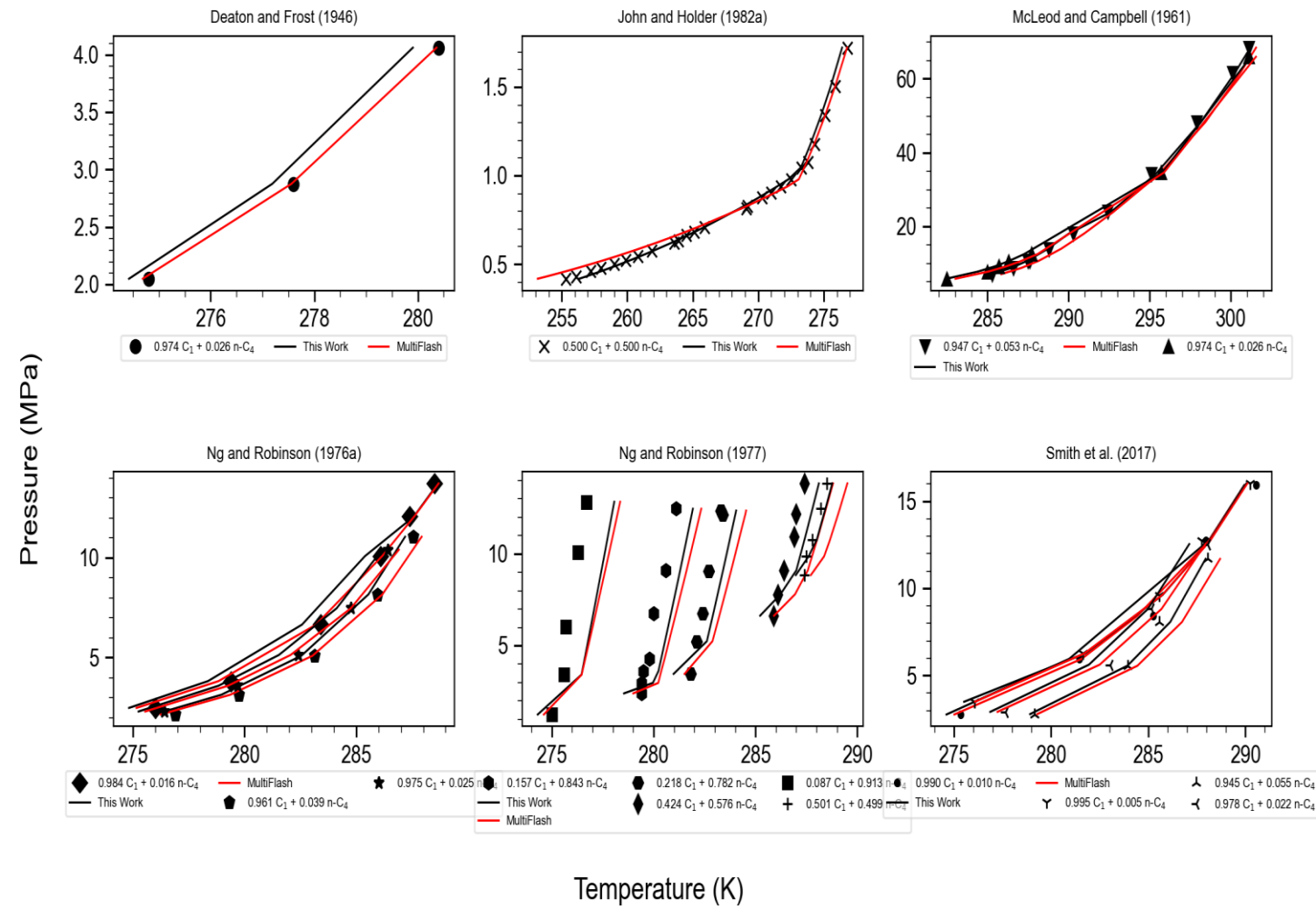


Figure S39: Selected hydrate equilibrium datasets $\text{CH}_4 + n\text{-C}_4\text{H}_{10}$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{16,40,137,165,176,177}

3.2.6. CH₄ + i-C₄H₁₀ binary-gas mixture hydrate equilibria

Table S27: Database of CH₄ + i-C₄H₁₀ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types:

'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AA DT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	x _{1,min}	x _{1,max}	N	Type
Deaton and Frost (1946) ¹⁶	Lw-H-V	II	0.193	0.037	1.166	274.8	277.6	1.324	1.841	0.9890	0.9890	2	Te
McLeod and Campbell (1961) ⁴⁰	Lw-H-V	II	1.329	0.761	0.616	288.6	305	6.72	63.33	0.9540	0.9860	20	Te
Ng and Robinson (1976) ¹⁶²	Lw-H-LHC	II	1.571	1.576	0.642	273.8	293.6	0.159	10.07	0.3490	0.9977	46	Te
Paranjpe et al. (1987) ¹³⁶	Lw-H-V- LHC	II	1.582	1.383	0.778	277	298.6	0.254	11.57	0.3490	0.9977	13	Te
Smith et al. (2017) ¹³⁷	Lw-H-V	II	0.659	0.616	0.533	275.4	299.3	0.179	14.548	0.0010	0.6470	38	Te
Thakore and Holder (1987) ⁵⁹	Lw-H-V	II	0.670	0.617	0.641	274.35	274.35	0.127	0.841	0.0360	0.9490	19	Te
Wu et al. (1976) ¹³³	Lw-H-V	II	0.683	0.596	0.539	276.2	281.2	0.2206	0.5851	0.2610	0.6200	3	Te
	Lw-H-V- LHC	II	1.015	0.763	0.322	281.25	297.45	2.745	15.524	0.9319	0.9941	15	Te
Overall/Test	—	—	1.121	0.988	0.597	273.8	305	0.127	63.33	0.0010	0.9977	156	—

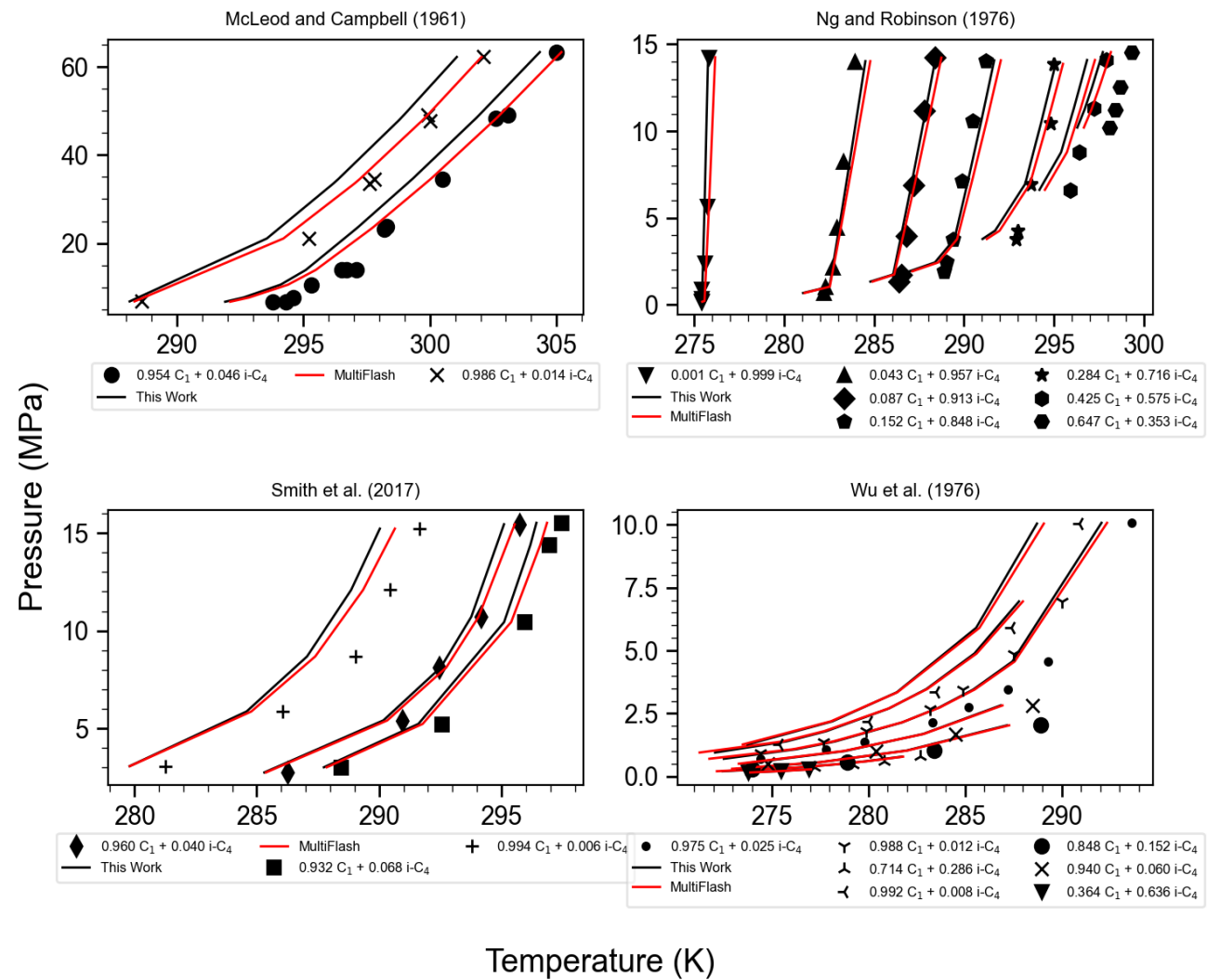


Figure S40: Selected hydrate equilibrium datasets $\text{CH}_4 + i\text{-C}_4\text{H}_{10}$ binary-gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{40,133,137,162}

3.2.7. $C_3H_8 + i-C_4H_{10}$ binary-gas mixture hydrate equilibria

Table S28: Database of $C_3H_8 + i-C_4H_{10}$ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types:

'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	$x_{1,min}$	$x_{1,max}$	N	Type
Kamath and Holder (1982) ¹⁷⁸	I-H-V	II	0.757	0.712	0.544	272.08	272.23	0.108	0.154	0.1250	0.9590	11	Te
Paranjpe et al. (1987) ¹³⁶	Lw-H-V- LHC	II	0.262	0.318	0.070	275.25	277.85	0.234	0.490	0.1120	0.7940	6	Te
Patil (1987) ¹¹⁹	Lw-H-V- LHC	II	0.263	0.320	0.070	275.25	277.85	0.213	0.491	0.1124	0.7935	6	Te
Overall/Test	—	—	0.499	0.507	0.297	272.08	277.85	0.108	0.491	0.1120	0.9590	23	—

3.2.8. $CO_2 + i-C_4H_{10}$ binary-gas mixture hydrate equilibria

Table S29: Database of $CO_2 + i-C_4H_{10}$ binary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. Data types:

'Tr' = Training data; 'Te' = Test data.

Reference	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	$x_{1,min}$	$x_{1,max}$	N	Type
Adisasmito and Sloan (1992) ¹⁶¹	Lw-H- V	II	1.005	0.636	1.254	273.7	280.9	0.145	3.179	0.207	0.996	43	Te
Adisasmito and Sloan (1992) ¹⁶¹	Lw-H- V	I	0.060	0.053	1.548	273.7	280.9	1.324	3.172	0.207	0.996	10	Te
Overall/Test	—	—	0.827	0.526	1.310	273.7	280.9	0.145	3.179	0.207	0.996	53	—

3.3. Ternary-gas and Multicomponent-gas hydrate equilibria

For ternary-gas mixture hydrate equilibria, for brevity we only plot the experimental datasets for $\text{CH}_4 + \text{C}_3\text{H}_8 + \text{H}_2\text{S}$ as these were used training the H_2S 5¹²6⁴ Kihara potential parameters in Figure S41. For multicomponent mixtures, a similar approach to binary-gas mixtures is used where only datasets with 3 or more points at a given composition are plotted on a pressure-temperature axis. The Deaton and Frost¹⁶ multicomponent datasets are split over three groups due to the numerous multicomponent mixtures measured.

Table S30: Database of ternary-gas mixture hydrate equilibrium data, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S. All of the data is test data, with the exception of the $\text{CH}_4 + \text{C}_3\text{H}_8 + \text{H}_2\text{S}$ data.

Reference	Mixtures	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N
Behnammotlagh et al. (2022) ¹⁷⁹	$\text{CH}_4 + \text{C}_3\text{H}_8 + \text{H}_2\text{S}$	Lw-H-V	II	0.159	0.536	0.186	284.25	296.05	2.29	12.08	5
Dharmawardhana et al. (1980) ¹⁸⁰	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$	Lw-H-V	I	0.530	0.213	0.167	279.76	283.98	1.25	2.275	8
	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$	Lw-H-V	II	0.559	0.600	0.532	275.76	282.04	0.92	1.882	3
Fan et al. (2019) ¹⁴⁹	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO}_2$	Lw-H-V	II	0.293	0.263	0.852	278.61	287.72	2.79	8.73	8
Holder and Hand (1982) ⁷³	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$	Lw-H-V-LHC	II	0.417	0.396	0.429	280.10	287.40	1.24	2.28	9
	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$	Lw-H-V-LHC	I	0.573	0.453	0.472	282.80	286.10	2.02	2.82	8
Legoix et al. (2018) ¹⁵⁴	$\text{CH}_4 + \text{N}_2 + \text{CO}_2$	Lw-H-V	I	1.016	0.725	0.689	282.46	288.62	9.68	15.645	5
Lim et al. (2017) ³⁶	$\text{CH}_4 + \text{N}_2 + \text{CO}_2$	Lw-H-V	I	0.309	0.485	0.557	279.60	293.00	4.81	30.66	30
Mohammadi and Richon (2015) ¹⁷⁴	$\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{S}$	Lw-H-V	I	0.369	0.208	0.288	274.20	280.60	0.88	1.71	5
Mu et al. (2018) ⁴³	$\text{CH}_4 + \text{N}_2 + \text{CO}_2$	Lw-H-V	I	0.097	0.217	0.042	276.98	283.84	2.84	7.005	6
Nixdorf and Oellrich (1997) ⁴⁶	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$	Lw-H-V	II	0.385	0.273	0.210	277.10	298.14	1.20	24.474	13
Nixdorf and Oellrich (1997) ⁴⁶	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{N}_2$	Lw-H-V	II	0.452	0.229	0.403	277.36	294.23	2.58	23.833	7
Obanijesu et al. (2014) ¹⁵⁵	$\text{CH}_4 + \text{N}_2 + \text{CO}_2$	Lw-H-V	I	4.818	4.705	4.633	281.95	286.45	10.00	20	5
Ovalle et al. (2022) ¹⁸¹	$\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$	Lw-H-V	II	0.150	0.242	0.110	277.49	285.82	1.24	3.5	5
	$\text{CH}_4 + \text{CO}_2 + \text{C}_3\text{H}_8$	Lw-H-V	II	0.570	0.605	0.350	277.98	287.96	1.25	4.75	5
Paranjpe et al. (1987) ¹³⁶	$\text{CH}_4 + \text{C}_3\text{H}_8 + i\text{-C}_4\text{H}_{10}$	Lw-H-V-LHC	II	0.223	0.233	0.291	276.20	281.20	0.25	0.7736	11
	$\text{CH}_4 + \text{C}_3\text{H}_8 + n\text{-C}_4\text{H}_{10}$	Lw-H-V-LHC	II	4.260	4.743	4.710	268.20	281.20	0.22	2.6438	10
Robinson and Hutton (1967) ¹⁸²	$\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{S}$	Lw-H-V	I	1.109	1.216	0.965	279.20	297.60	1.48	15.707	34
Sabil et al. (2014) ⁵²	$\text{CH}_4 + \text{N}_2 + \text{CO}_2$	Lw-H-V	I	1.732	1.919	1.852	280.65	289.86	2.71	12.1	7
Schroeter et al. (1983) ¹⁸³	$\text{CH}_4 + \text{C}_3\text{H}_8 + \text{H}_2\text{S}$	Lw-H-V	II	0.560	0.333	2.613	275.85	300.95	0.34	4.274751	13
Smith et al. (2017) ¹³⁷	$\text{N}_2 + \text{CH}_4 + \text{C}_3\text{H}_8$	Lw-H-V	II	0.883	0.529	0.882	284.15	294.75	2.89	16.027	5
	$\text{N}_2 + \text{CH}_4 + i\text{-C}_4\text{H}_{10}$	Lw-H-V	II	0.604	0.385	0.255	286.35	295.85	3.19	14.963	4
	$\text{N}_2 + \text{CH}_4 + n\text{-C}_4\text{H}_{10}$	Lw-H-V	II	0.469	0.812	0.582	277.95	286.45	2.75	12.09	4

Reference	Mixtures	Phases	Structure	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N
Sun et al. (2003) ¹⁸⁴	CH ₄ + CO ₂ + H ₂ S	Lw-H-V	I	0.925	0.724	0.849	274.20	299.70	0.58	8.68	59
Sun et al. (2016) ¹⁰⁸	CH ₄ + N ₂ + CO ₂	Lw-H-V	I	0.051	0.042	0.055	276.15	278.15	2.14	2.744	9
Sun et al. (2017) ¹⁸⁵	CH ₄ + N ₂ + CO ₂	Lw-H-V	I	0.378	0.305	0.334	274.90	283.90	2.29	14.97	45
Sun Zhi-Gao (2001) ¹⁸⁶	CH ₄ + C ₂ H ₆ + C ₃ H ₈	Lw-H-V	II	0.271	0.282	0.288	273.58	288.96	0.91	5.37	7
Ward et al. (2015a) ¹⁷⁵	CH ₄ + C ₃ H ₈ + H ₂ S	Lw-H-V	II	0.609	1.522	1.691	286.22	304.80	1.36	6.89	10
Zang and Liang (2018) ¹⁸⁷	CH ₄ + N ₂ + CO ₂	Lw-H-V	I	0.477	0.398	0.496	276.20	286.30	2.59	8.84	34
Overall	—	—	—	0.742	0.730	0.838	268.20	304.80	0.22	30.66	374

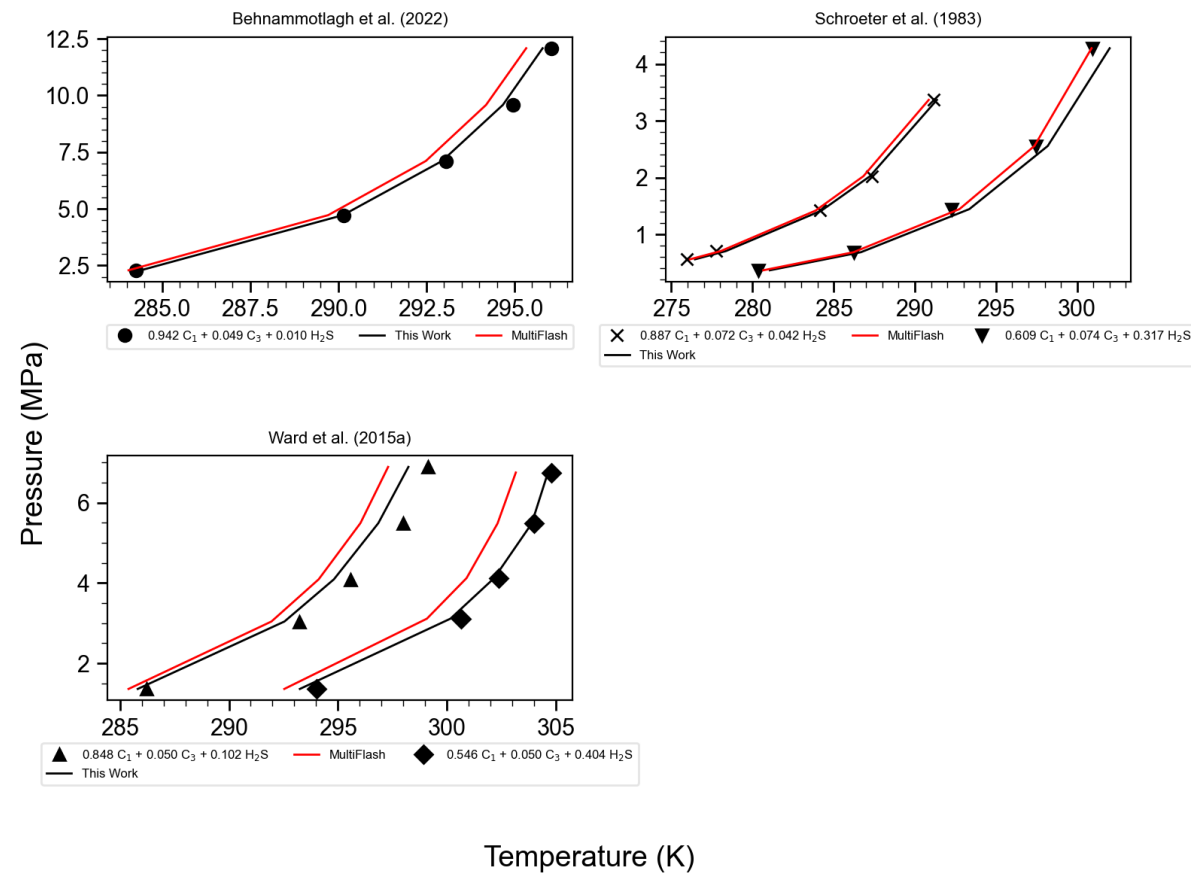


Figure S41: Selected hydrate equilibrium datasets for CH₄ + C₃H₈ + H₂S ternary gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{175,179,183}

Table S31: Database of multicomponent-gas-mixture hydrate equilibrium data with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S.

Reference	Mixtures	Phases	Structure	AA DT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N
Adisasmito and Sloan (1992) ¹⁶¹	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀	Lw-H-V	II	0.484	0.562	0.653	273.70	282.00	0.4966	1.4138	4
	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , CO ₂	Lw-H-V	II	0.868	0.772	0.846	273.70	282.00	0.5931	3.5103	12
	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , CO ₂	Lw-H-V	I	0.227	0.210	0.316	273.70	282.00	1.3379	3.469	4
Cha et al. (2013) ¹⁸⁸	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , n-C ₄ H ₁₀	Lw-H-V	II	0.946	0.981	0.760	289.60	294.70	5.2	11.3	3
Deaton and Frost (1946) ¹⁶	N ₂ , CO ₂ , CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀	Lw-H-V	II	1.068	1.026	1.198	273.70	294.00	0.6	9.391	75
	N ₂ , CO ₂ , H ₂ S, CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀	Lw-H-V	II	0.497	0.433	0.685	275.40	289.30	0.945	5.254	4
	N ₂ , CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀	Lw-H-V	II	1.375	1.317	1.701	273.70	291.50	0.758	7.729	11
	N ₂ , CO ₂ , CH ₄ , C ₂ H ₆ , C ₃ H ₈	Lw-H-V	II	1.398	1.198	1.810	273.70	289.80	1.262	10.439	9
Fan and Guo (1999) ⁸⁷	CH ₄ , C ₂ H ₆ , CO ₂ , N ₂	Lw-H-V	I	0.396	0.299	0.268	272.80	279.30	1.16	2.77	5
Kobayashi et al. (1951) ¹⁸⁹	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , n-C ₅ H ₁₂ , n-C ₆ H ₁₄ , N ₂	Lw-H-V	II	1.326	1.355	1.427	283.30	291.00	2.186	5.661	5
	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , n-C ₅ H ₁₂ , N ₂	Lw-H-V	II	1.078	1.184	1.256	281.60	290.90	1.765	5.583	5
Lee and Kang (2011) ¹⁹⁰	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , N ₂	Lw-H-V	II	0.990	1.040	0.892	281.40	291.40	1.71	6.61	5
McLeod and Campbell (1961) ⁴⁰	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀	Lw-H-V	II	0.339	0.829	0.876	293.60	303.10	13.55	62.85	7
Mei et al. (1998) ¹⁹¹	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀	Lw-H-V	II	1.861	2.095	1.462	273.50	281.90	0.92	2.67	8
Ng and Robinson (1976) ¹⁶²	C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , N ₂	Lw-H-V	II	0.257	0.070	0.587	277.70	277.80	1.158	9.714	7
	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , N ₂	Lw-H-V	II	0.115	0.110	0.410	281.20	293.90	1.565	13.623	13
	C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , CO ₂	Lw-H-V	II	1.621	0.240	0.771	274.80	285.70	0.689	14.7	14
	C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , i-C ₅ H ₁₂	Lw-H-V	II	0.332	0.310	0.879	274.80	275.60	0.689	11.893	5
Nixdorf and Oellrich (1997) ⁴⁶	CH ₄ , C ₃ H ₈ , N ₂ , CO ₂	Lw-H-V	II	0.895	1.034	0.533	279.19	296.07	1.693	23.565	6
	CH ₄ , C ₂ H ₆ , N ₂ , CO ₂	Lw-H-V	II	0.348	0.232	0.599	279.01	294.21	2.964	24.326	6
Saberi et al. (2018) ⁵¹	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , N ₂ , CO ₂	Lw-H-V	II	0.874	0.922	0.907	289.90	294.50	3.95	8.2	6
Sabil et al. (2014) ⁵²	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , N ₂ , CO ₂	Lw-H-V	I	1.964	2.125	2.106	280.95	290.15	2.75	12.5	11
Wilcox et al. (1941) ¹⁹²	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , N ₂ , CO ₂	Lw-H-V	II	0.200	0.292	0.332	277.70	296.70	1.6	27.503	15
	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , i-C ₄ H ₁₀ , n-C ₄ H ₁₀ , C ₅ H ₁₂ , N ₂	Lw-H-V	II	0.318	0.442	0.365	278.80	298.30	1.255	27.32	9
Overall	—	—	—	0.923	0.855	1.001	272.80	303.10	0.4966	62.85	249

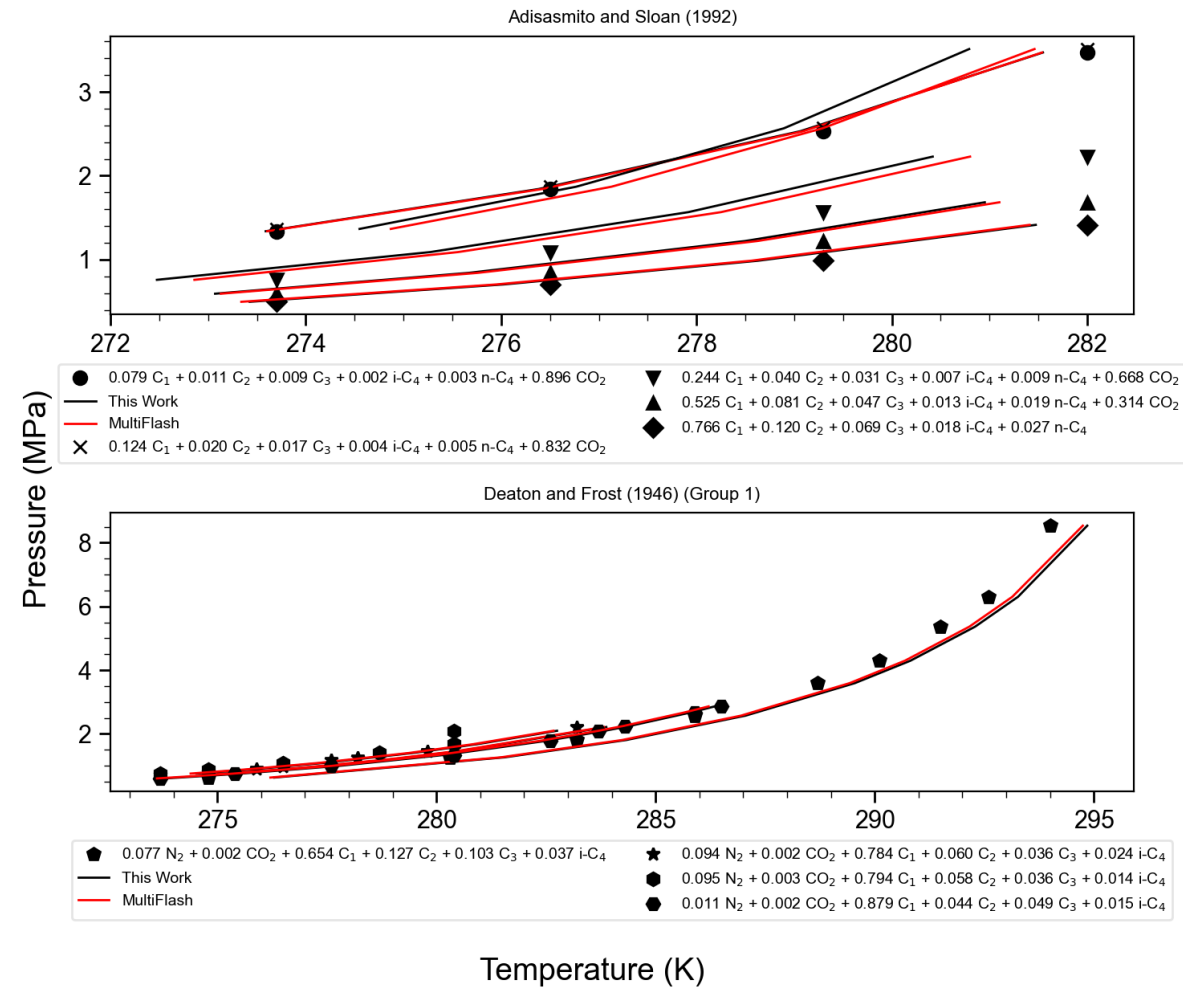


Figure S42: Selected hydrate equilibrium datasets for multicomponent gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{16,161}, with water-free compositions labelled in the figure legends.

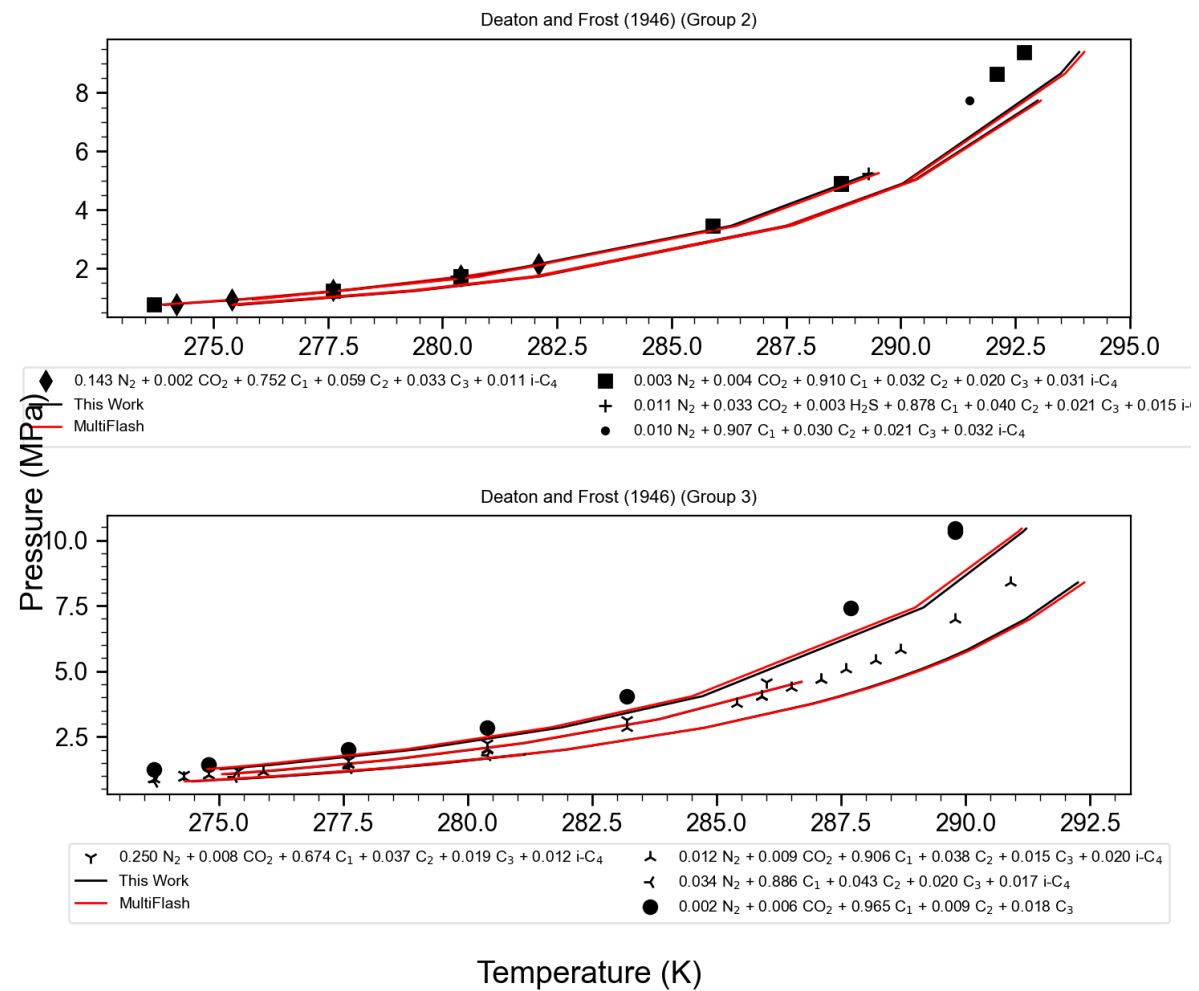


Figure S43: Selected hydrate equilibrium datasets for multicomponent gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:¹⁶, with water-free compositions labelled in the figure legends.

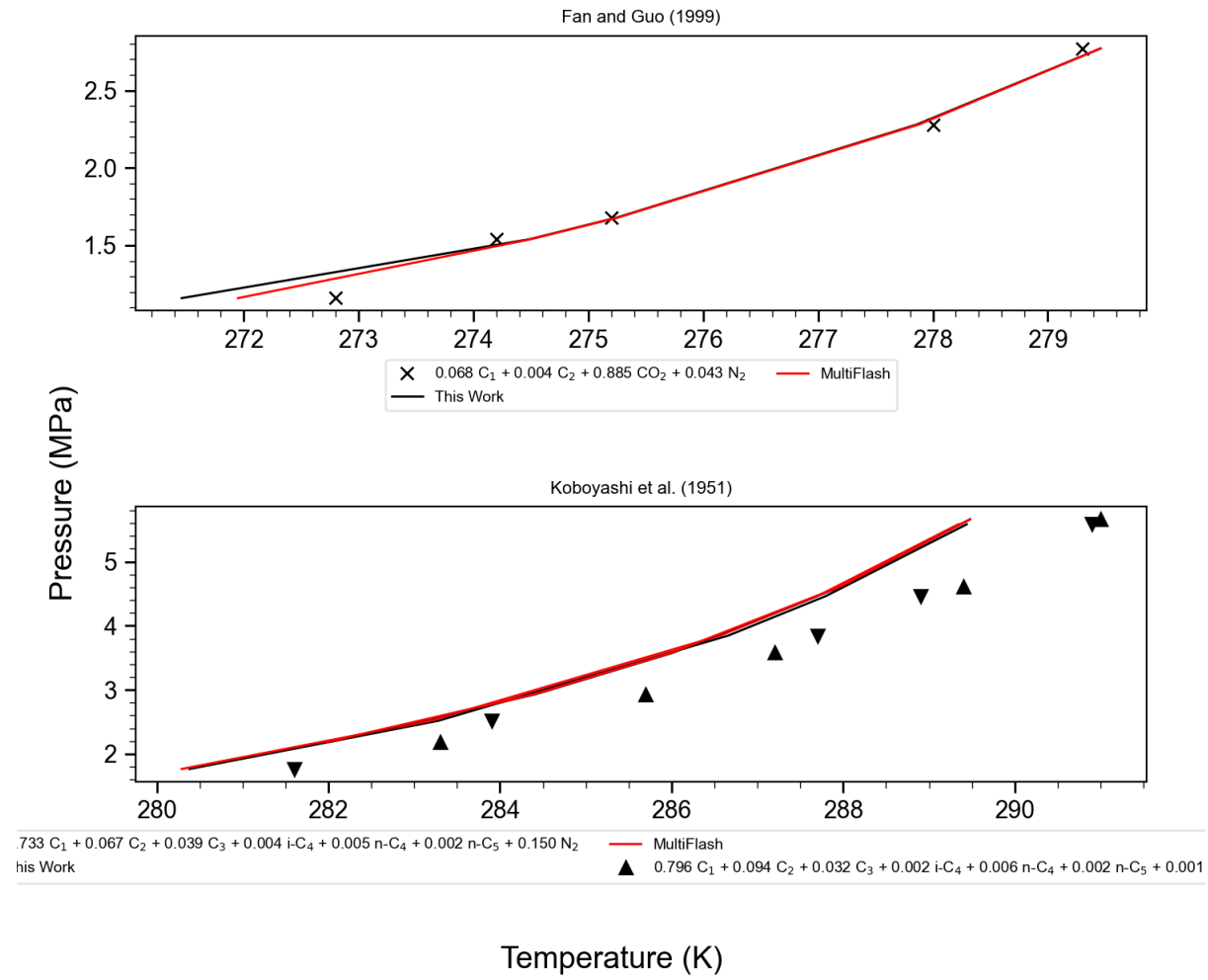


Figure S44: Selected hydrate equilibrium datasets for multicomponent gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{87,189}, with water-free compositions labelled in the figure legends.

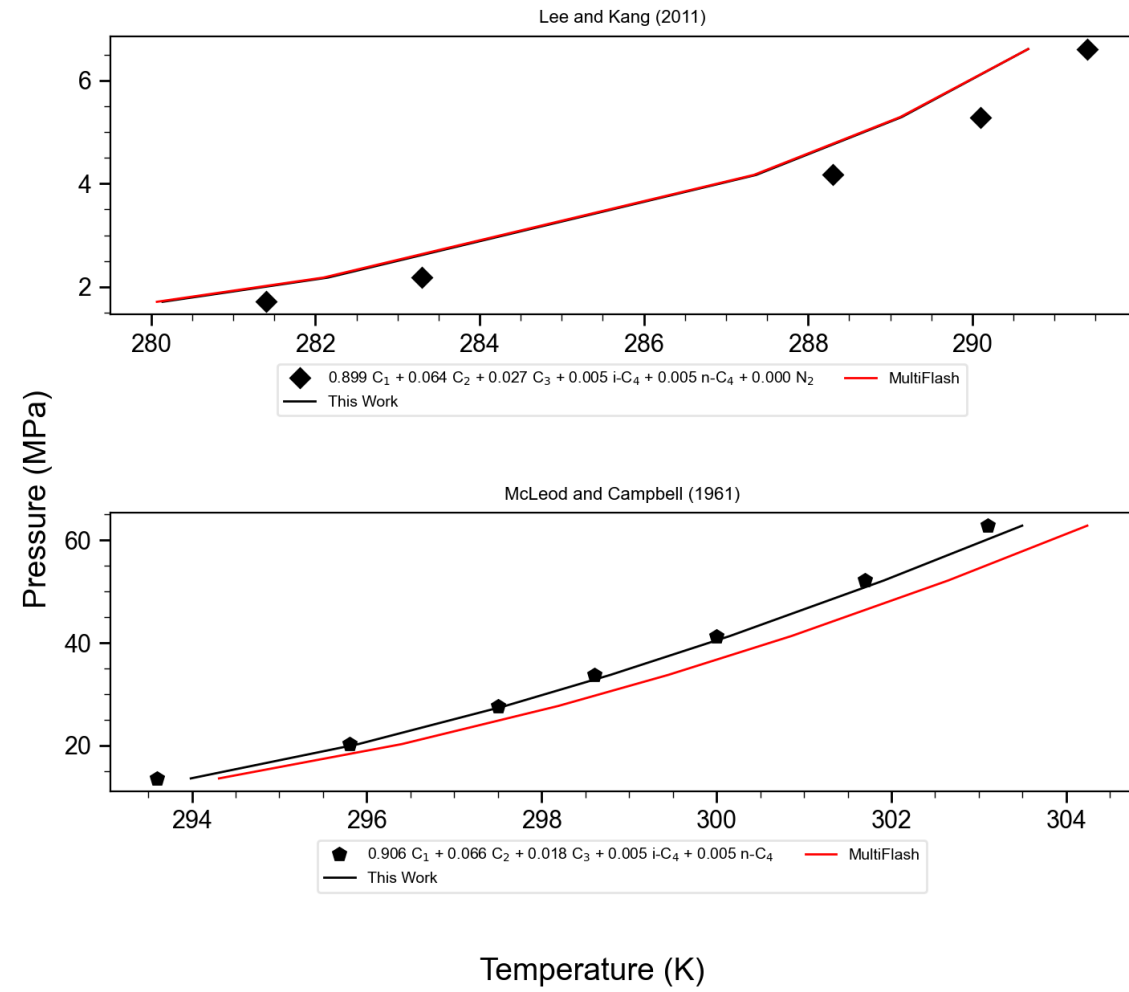


Figure S45: Selected hydrate equilibrium datasets for multicomponent gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{40,190}, with water-free compositions labelled in the figure legends.

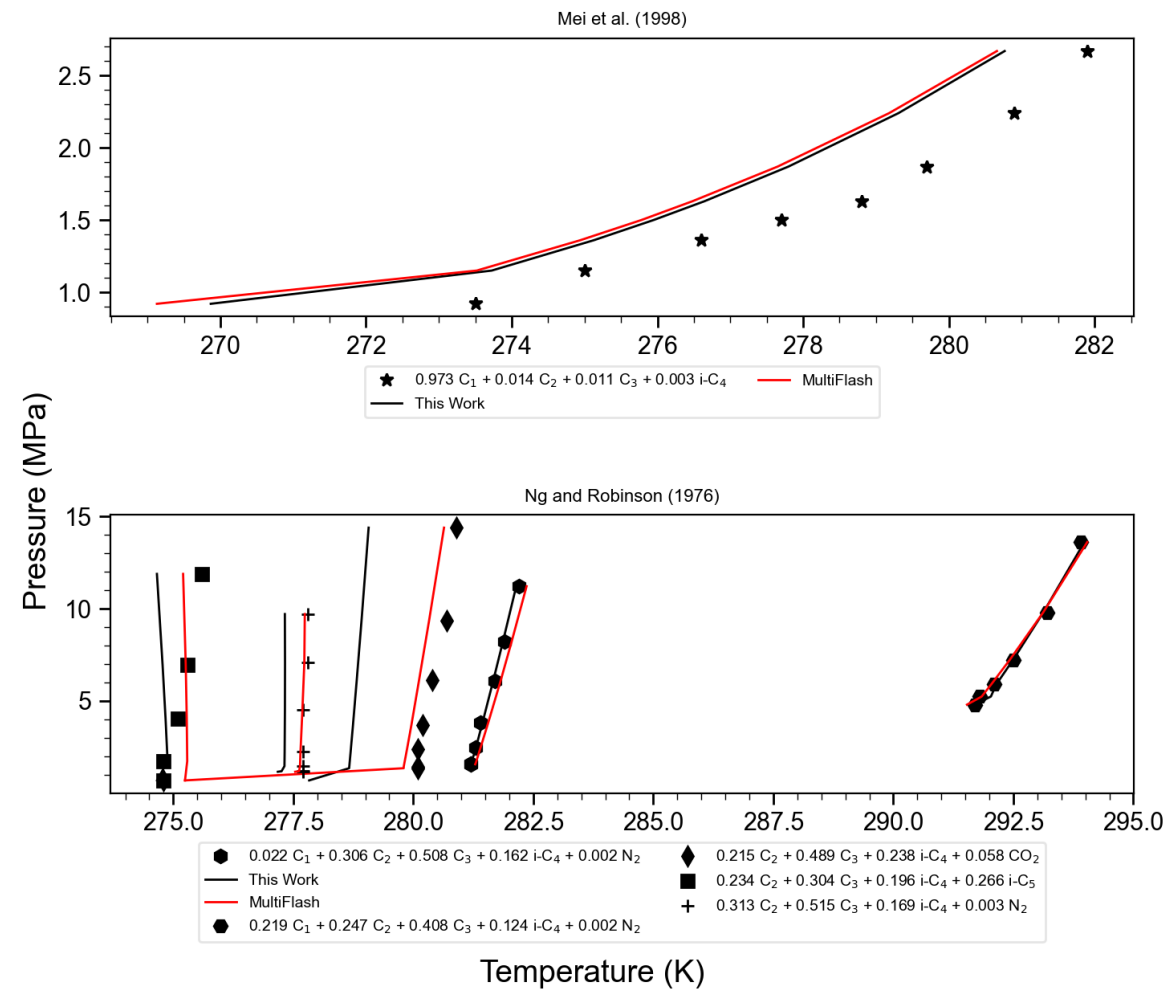


Figure S46: Selected hydrate equilibrium datasets for multicomponent gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{162,191}, with water-free compositions labelled in the figure legends.

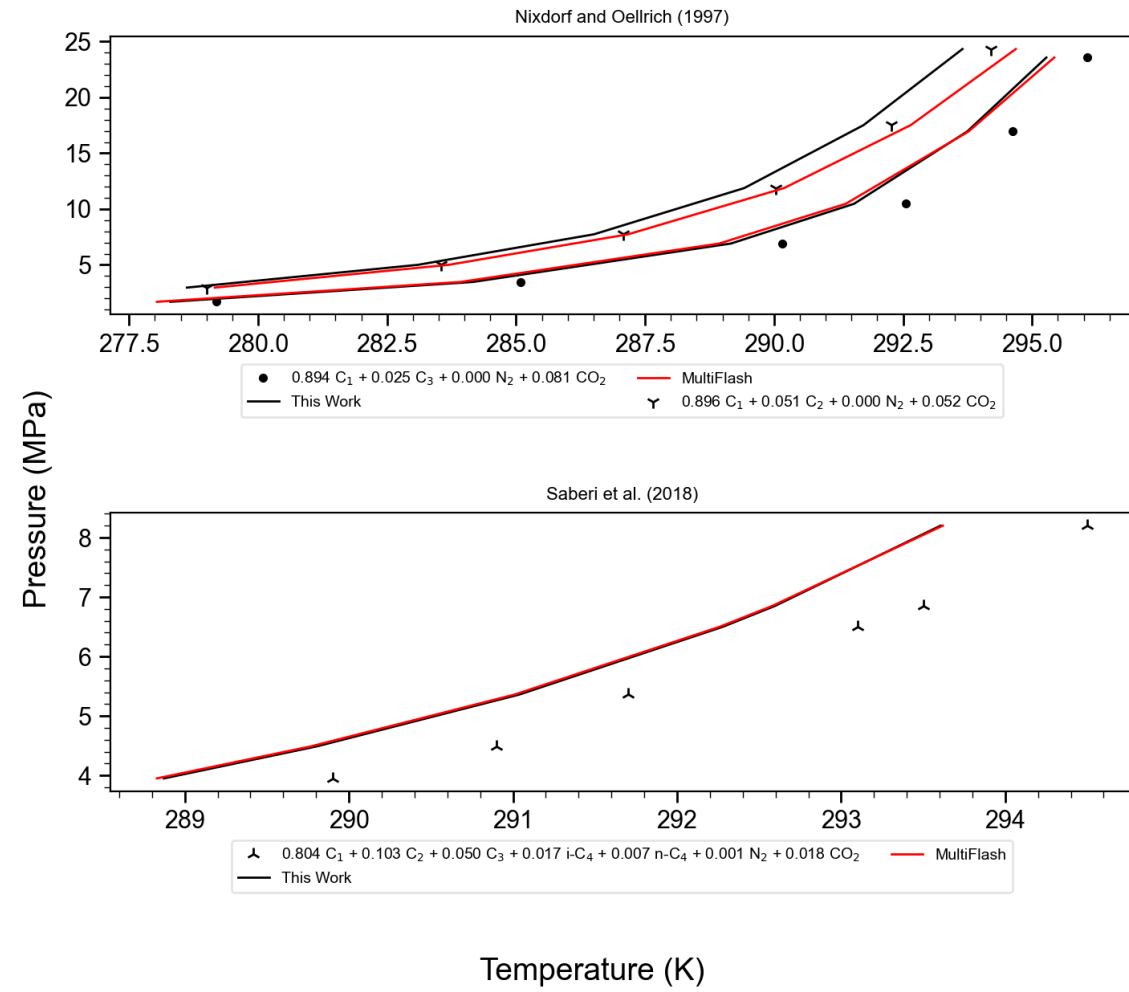


Figure S47: Selected hydrate equilibrium datasets for multicomponent gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{46,51}, with water-free compositions labelled in the figure legends.

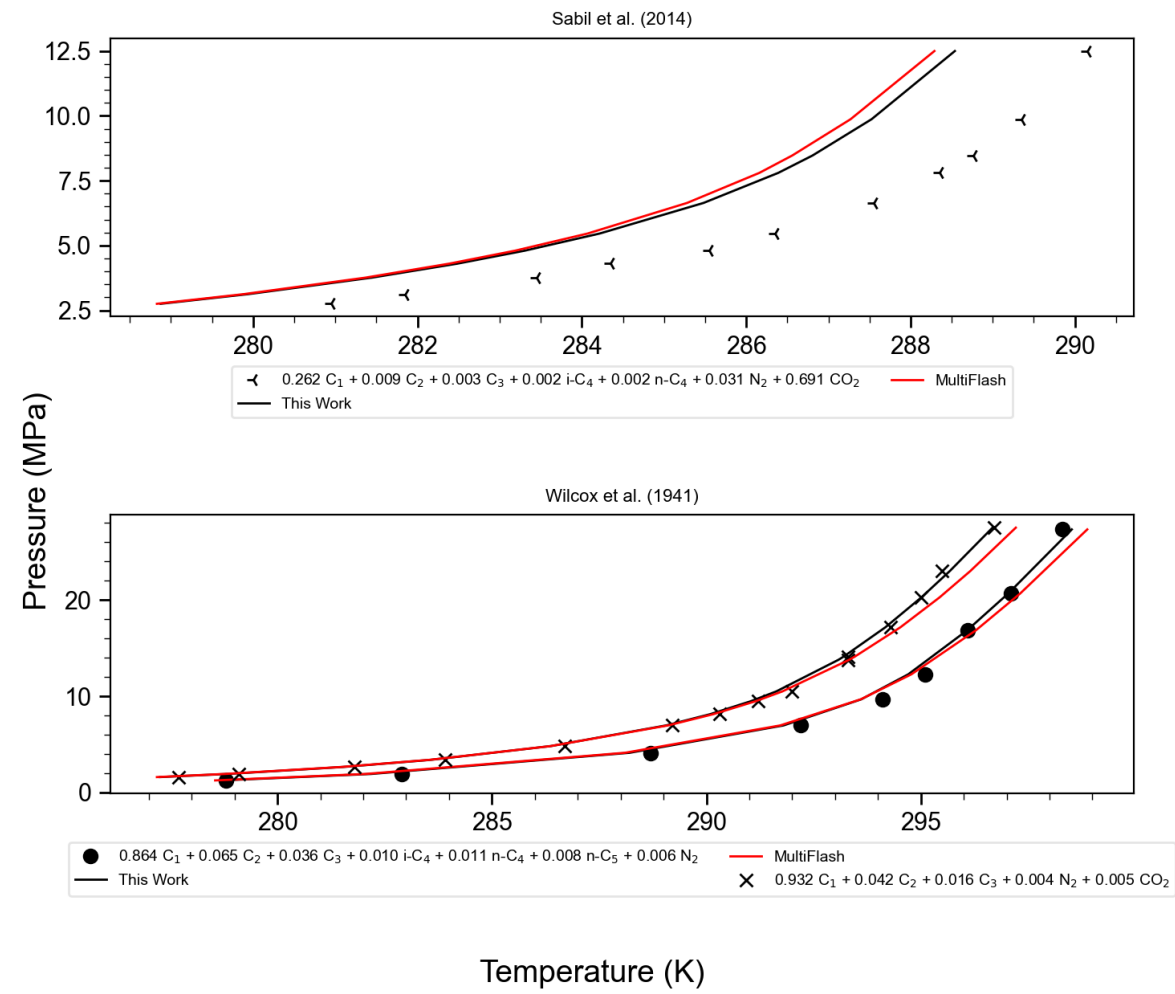


Figure S48: Selected hydrate equilibrium datasets for multicomponent gas mixture hydrates, along with the predictions from two models: the CaSH model (black) and the MultiFlash 7.0 CPA-Hydrates (red). Datasets:^{52,192}, with water-free compositions labelled in the figure legends.

3.4. Inhibited hydrate equilibria

Table S32: Database of simple methane hydrate equilibria systems inhibited with MEG at varying wt% dosages, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S.

Reference	MEG wt%	Phases	AADT (K)	CPAHYD-MF AADT (K)	B&S AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	N
Robinson and Ng (1986) ¹⁹³	10	Lw-H-V	0.297	0.402	0.165	270.2	287.1	2.42	15.6	4
	30	Lw-H-V	0.705	0.506	0.183	267.6	280.1	3.77	16.38	5
	50	Lw-H-V	0.776	0.180	2.128	263.4	266.5	9.89	15.24	3
Eichholz et al. (2004) ¹⁹⁴	19.16	Lw-H-V	0.834	0.926	0.299	266.5	279.5	2.136	8.62	3
Mohammadi and Richon (2011a) ¹⁹⁵	65	Lw-H-V	0.802	0.750	7.517	247.4	250.7	10.38	18.32	3
Haghighi et al. (2009a) ¹⁹⁶	10	Lw-H-V	0.046	0.121	0.112	279.4	293.95	6.379	37.448	3
	20	Lw-H-V	0.558	0.319	0.346	277.75	289.25	7.159	29.917	3
	30	Lw-H-V	0.828	0.438	0.193	273.35	284.8	6.862	31.69	3
	40	Lw-H-V	0.972	0.362	0.605	264.95	279.05	5.055	31.386	4
	50	Lw-H-V	1.151	0.285	2.582	265.35	271.55	12.621	30.91	3
Mohammadi and Richon (2010b) ¹⁹⁷	6.9	Lw-H-V	0.239	0.172	0.345	271.8	284.7	2.79	10.42	10
	10	Lw-H-V	0.216	0.261	0.183	271.9	283.4	2.91	9.93	5
	20	Lw-H-V	0.827	0.844	0.396	270.4	279.8	3.06	9.41	4
	35	Lw-H-V	1.068	0.861	0.410	268.5	274.6	5.31	10.62	4
	50	Lw-H-V	0.597	0.266	1.551	258.7	263.7	5.67	10.11	4
Overall	—	—	0.607	0.419	0.940	247.4	293.95	2.136	37.448	61

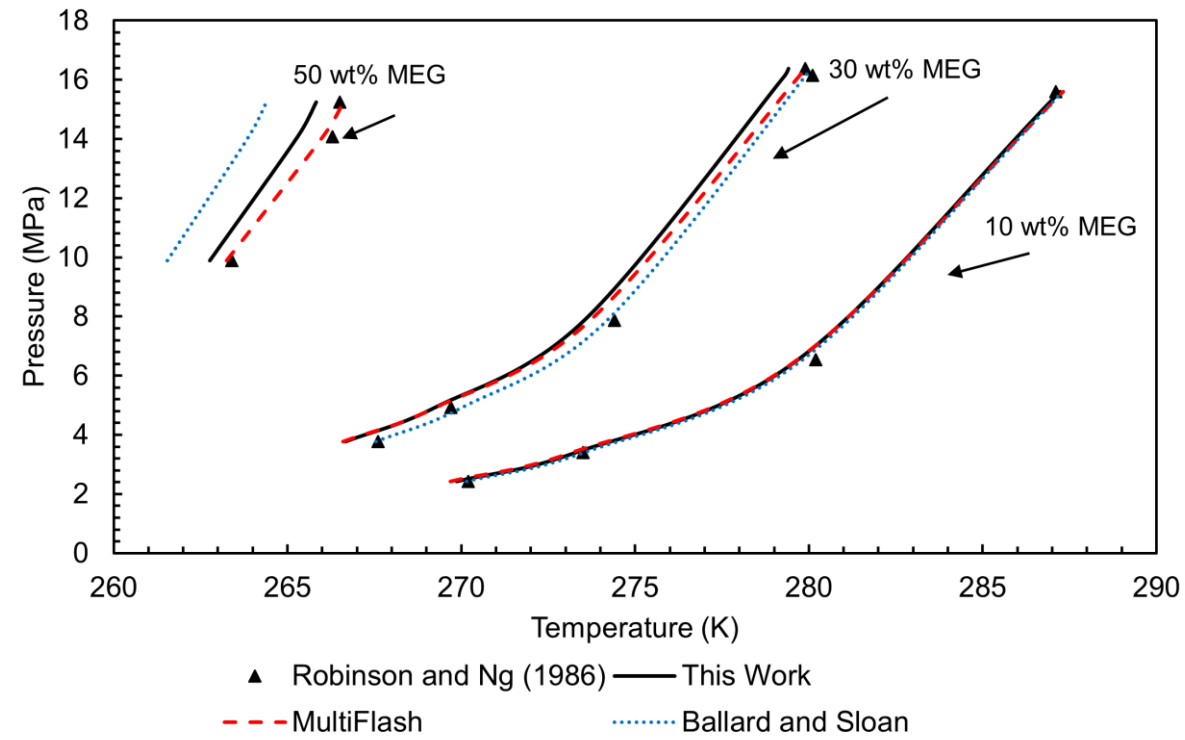


Figure S49: Selected hydrate equilibrium datasets for methane simple hydrates inhibited with MEG at varying wt%, along with the predictions from three models: the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Datasets:¹⁹³

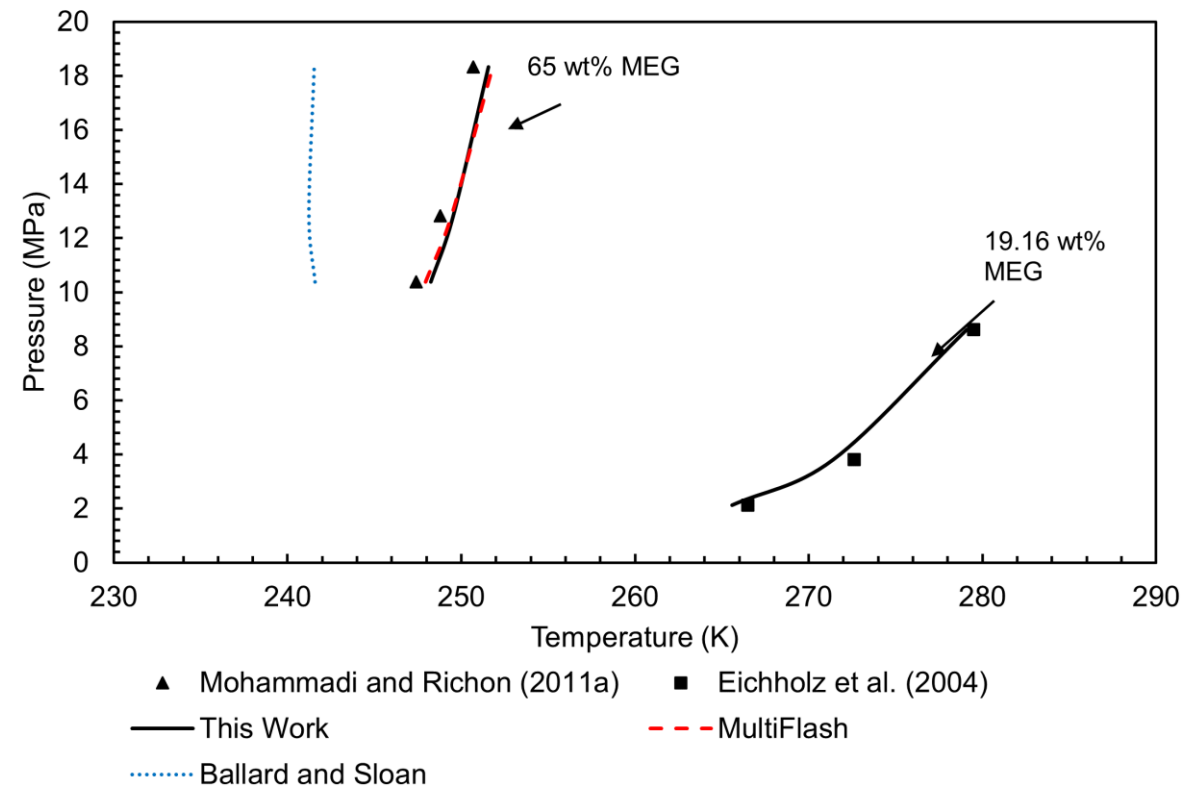


Figure S50: Selected hydrate equilibrium datasets for methane simple hydrates inhibited with MEG at varying wt%, along with the predictions from three models: the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Datasets:^{194,195}

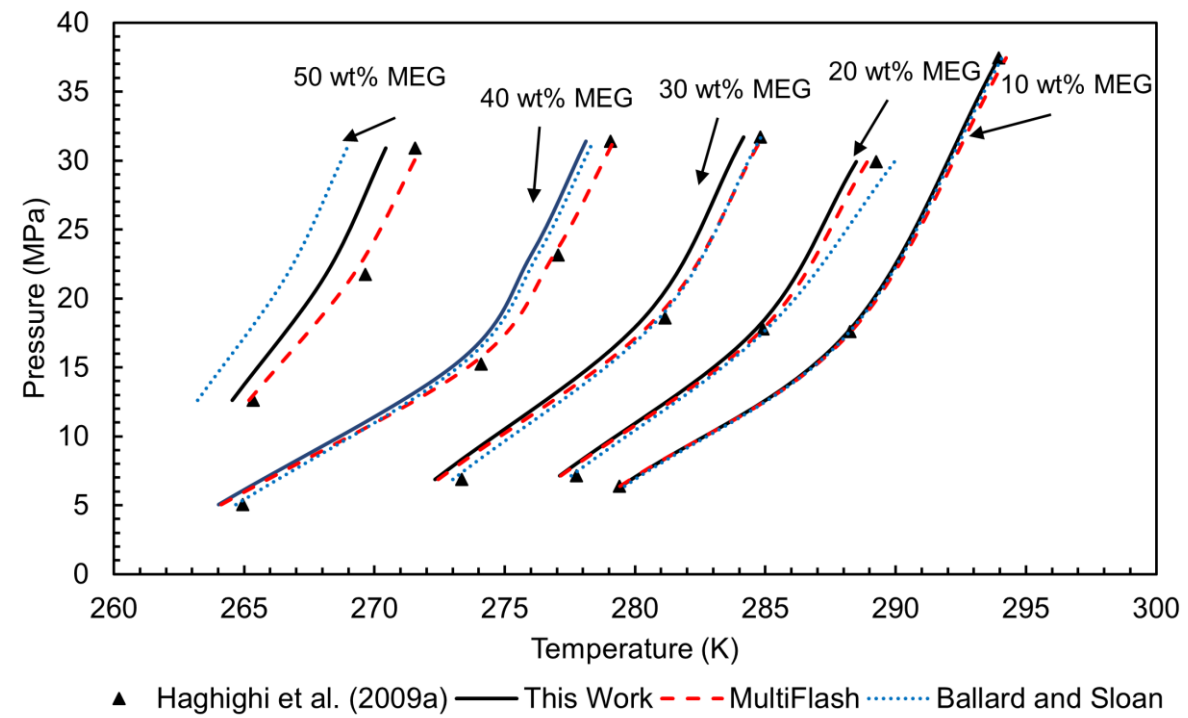


Figure S51: Selected hydrate equilibrium datasets for methane simple hydrates inhibited with MEG at varying wt%, along with the predictions from three models: the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Datasets:¹⁹⁶

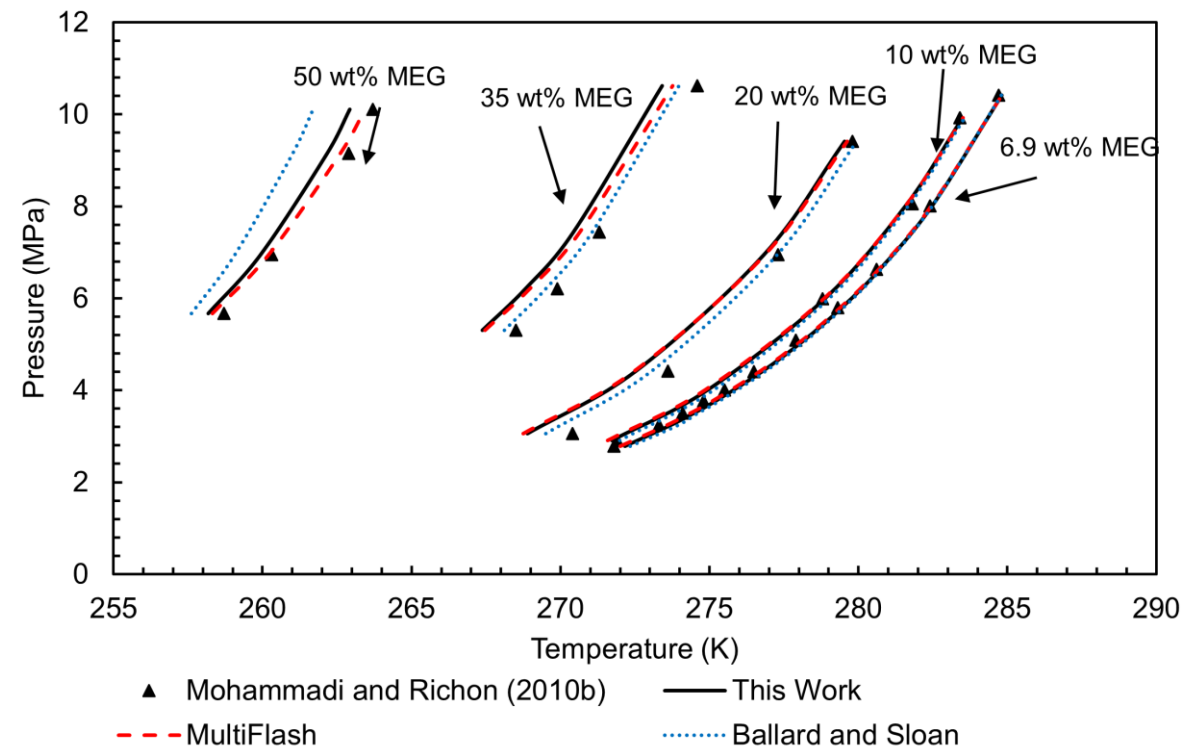


Figure S52: Selected hydrate equilibrium datasets for methane simple hydrates inhibited with MEG at varying wt%, along with the predictions from three models: the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Datasets:¹⁹⁷

Table S33: Database of binary-gas-mixture hydrate equilibrium systems inhibited with MEG at varying wt% dosages, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S.

Reference	Mixtures	MEG wt%	Phases	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	x_{1+min}	x_{1+max}	N
Fan et al. (2000) ⁸⁸	CH ₄ + CO ₂	10	Lw-H-V	1.214	1.190	1.192	268.7	278	1.14	3.22	0.0348	0.0348	4
	N ₂ + CO ₂	10	Lw-H-V	0.549	0.542	0.416	268.9	276.1	1	2.49	0.0348	0.0348	4
	C ₂ H ₆ + CO ₂	10.6	Lw-H-V	0.802	0.659	0.737	269.1	276.4	0.85	2.31	0.0531	0.0531	5
	N ₂ + CO ₂	13.01	Lw-H-V	0.791	0.736	0.555	267.2	276.5	0.93	3.39	0.0901	0.0901	8
Hemmingsen et al. (2011) ¹³⁴	CH ₄ + C ₃ H ₈	40	Lw-H-V	1.297	1.428	0.985	267.95	283.35	1.22	13.33	0.8813	0.8813	3
	CH ₄ + C ₃ H ₈	50	Lw-H-V	1.660	1.618	3.147	267.95	277.45	2.25	17.49	0.8813	0.8813	3
	CH ₄ + C ₃ H ₈	60	Lw-H-V	0.861	1.067	6.200	258.85	267.85	2.36	17.27	0.8813	0.8813	3
Dholabhai et al. (1997) ¹⁹⁸	CH ₄ + CO ₂	10	Lw-H-V	0.242	0.396	0.120	269.57	281.22	1.92	6.318	0.813	0.858	3
	CH ₄ + CO ₂	30	Lw-H-V	0.962	1.030	0.440	264.78	277.17	2.428	9.167	0.815	0.864	3
Aminolroayaei et al. (2022) ¹⁹⁹	CH ₄ + H ₂ S	10	Lw-H-V	0.717	0.655	0.817	280.55	286.05	6.56	12.29	0.99	0.99	4
	CH ₄ + H ₂ S	15	Lw-H-V	0.149	0.118	0.387	281.58	284.67	8.16	12	0.99	0.99	3
	CH ₄ + H ₂ S	20	Lw-H-V	0.721	0.732	1.169	276.65	282.65	6.28	11.78	0.99	0.99	4
Overall	—	—	—	0.823	0.822	1.199	258.85	286.05	0.85	17.49	—	—	47

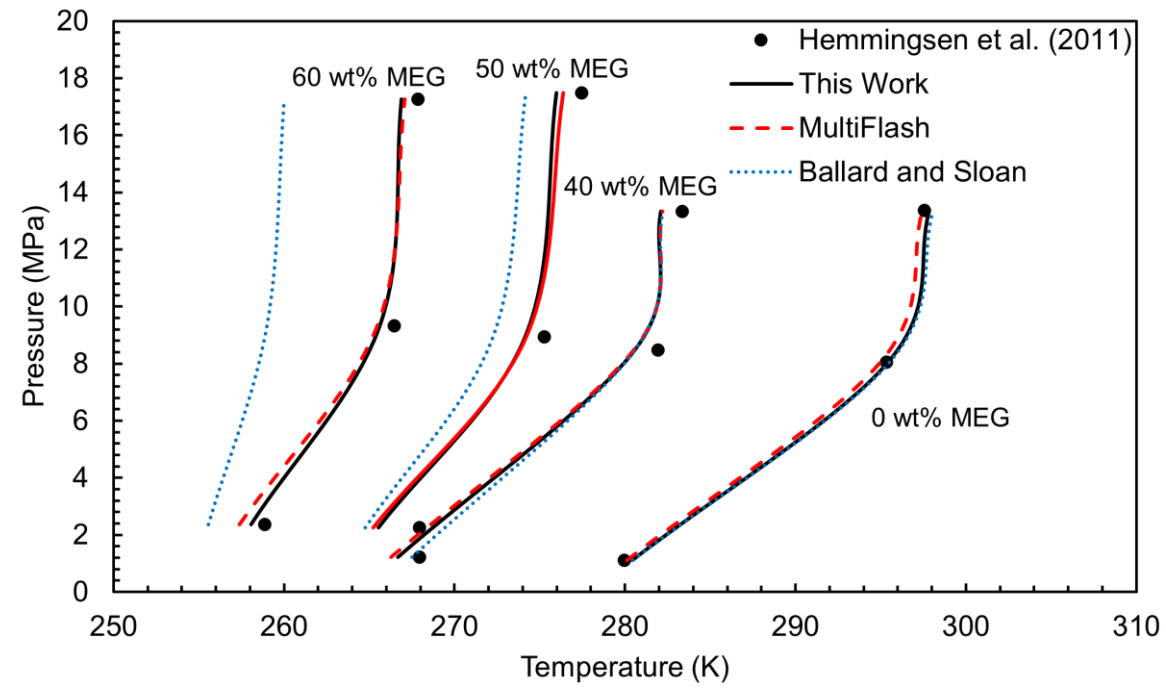


Figure S53: Selected hydrate equilibrium datasets for binary-gas mixture hydrates inhibited with MEG at varying wt%, along with the predictions from three models: the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Datasets:¹³⁴ - 0.8813 CH₄ + 0.1187 C₃H₈ (water-free molar composition)

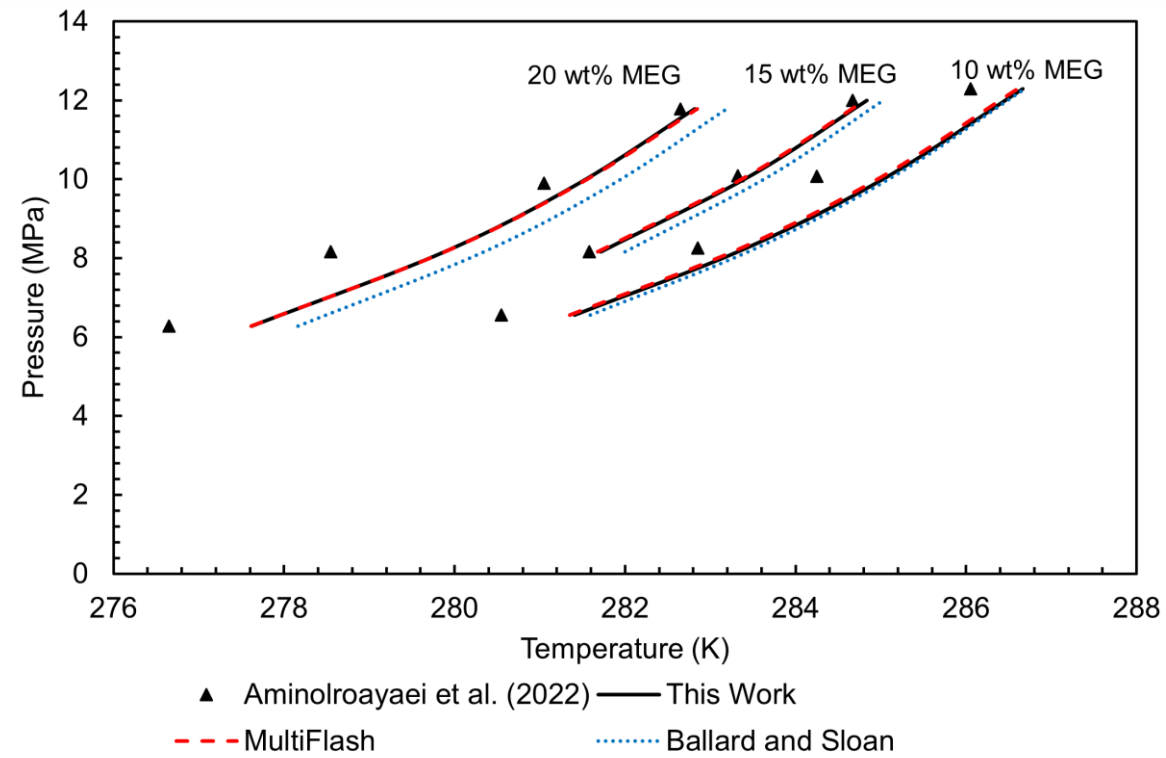


Figure S54: Selected hydrate equilibrium datasets for binary-gas mixture hydrates inhibited with MEG at varying wt%, along with the predictions from three models: the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Datasets:¹⁹⁹ - 0.99 CH₄ + 0.01 H₂S (water-free molar composition)

Table S34: Database of multicomponent gas mixture hydrate equilibria systems inhibited with MEG at varying wt % dosages, with comparison of the AADT of the cavity-based hydrate model with CPAHYD-MF and B&S.

Reference	Mixtures	MEG wt%	Phases	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N
Cha et al. (2013) ¹⁸⁸	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + n-C ₄ H ₁₀	10	Lw-H- V	1.124	1.185	3.084	286.8	291.7	4.8	10	3
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + n-C ₄ H ₁₀	30	Lw-H- V	1.762	1.703	3.434	281.5	284.9	5	11.4	3
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + n-C ₄ H ₁₀	50	Lw-H- V	0.804	0.602	4.809	269.7	271.9	5.7	11.4	4
Fan et al. (2000) 10 wt% MEG ⁸⁸	CH ₄ + C ₂ H ₆ + N ₂ + CO ₂	10	Lw-H- V	1.825	1.826	1.672	268.8	279.3	0.8	3.5	6
Haghighi et al. (2009) ²⁰⁰	N ₂ + CO ₂ + CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + i-C ₅ H ₁₂ + n-C ₅ H ₁₂ + n-C ₆ H ₁₄ + n-C ₇ H ₁₆	10	Lw-H- V	0.062	0.194	0.369	280.25	292.75	2.78	20.26	3
	N ₂ + CO ₂ + CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + i-C ₅ H ₁₂ + n-C ₅ H ₁₂ + n-C ₆ H ₁₄ + n-C ₇ H ₁₆	30	Lw-H- V	0.535	0.247	0.488	276.55	287.45	3.999	29.82	4
	N ₂ + CO ₂ + CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + i-C ₅ H ₁₂ + n-C ₅ H ₁₂	50	Lw-H- V	0.762	0.876	2.036	258.85	275.15	1.855	35.763	4
Lee and Kang (2011) ¹⁹⁰	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂	10	Lw-H- V	0.765	0.686	1.009	275.7	289.2	1.52	8.22	5
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂	20	Lw-H- V	0.262	0.338	0.254	271.1	287.7	1.09	9.2	5
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂	30	Lw-H- V	0.472	0.448	0.627	266.2	283.7	0.99	8.64	5
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂	40	Lw-H- V	1.974	1.832	2.388	261.2	275.8	1.28	8.15	5
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂	50	Lw-H- V	1.308	1.385	0.555	264.6	270.2	4.04	9.21	4
Nasir et al. (2014) ²⁰¹	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂ + CO ₂	10	Lw-H- V	0.259	0.304	0.201	278.15	284.75	3.21	10.06	5
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂ + CO ₂	20	Lw-H- V	0.440	0.570	0.352	276.15	282.05	3.58	10.82	5

Reference	Mixtures	MEG wt%	Phases	AADT (K)	MF AADT (K)	CSMGem AADT (K)	T _{min} (K)	T _{max} (K)	P _{min} (MPa)	P _{max} (MPa)	N
Saberi et al. (2018) ⁵¹	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂ + CO ₂	10	Lw-H-V	0.739	0.790	1.007	290.2	292.1	6.03	8.34	4
	CH ₄ + C ₂ H ₆ + C ₃ H ₈ + i-C ₄ H ₁₀ + n-C ₄ H ₁₀ + N ₂ + CO ₂	20	Lw-H-V	1.318	1.345	1.445	287.3	289.6	5.87	8.91	4
Overall	—	—	—	0.913	0.899	1.404	258.85	292.75	0.8	35.763	70

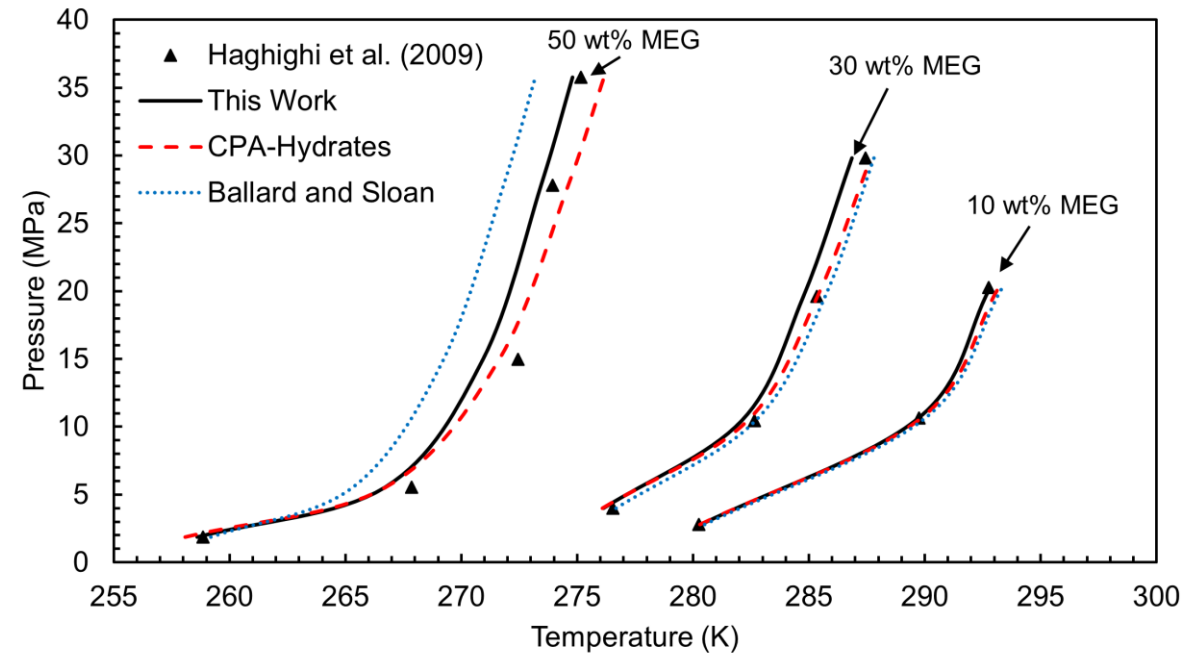


Figure S55: Experimental hydrate equilibrium data of a multicomponent gas mixture at different wt% of MEG, alongside predictions from the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). (Note - Same as Figure S10 in main manuscript) Dataset:¹⁹⁶ - water-free molar composition (10 wt% MEG, 30 wt% MEG): 0.8821 CH₄ + 0.0578 C₂H₆ + 0.0178 C₃H₈ + 0.0019 i-C₄H₁₀ + 0.0006 i-C₅H₁₂ + 0.0007 n-C₅H₁₂ + 0.0001 n-C₇H₁₆ + 0.014 N₂ + 0.0215 CO₂; (50 wt% MEG): 0.883 CH₄ + 0.054 C₂H₆ + 0.015 C₃H₈ + 0.002 i-C₄H₁₀ + 0.003 n-C₄H₁₀ + 0.001 i-C₅H₁₂ + 0.0009 n-C₅H₁₂ + 0.0239 N₂ + 0.0172 CO₂

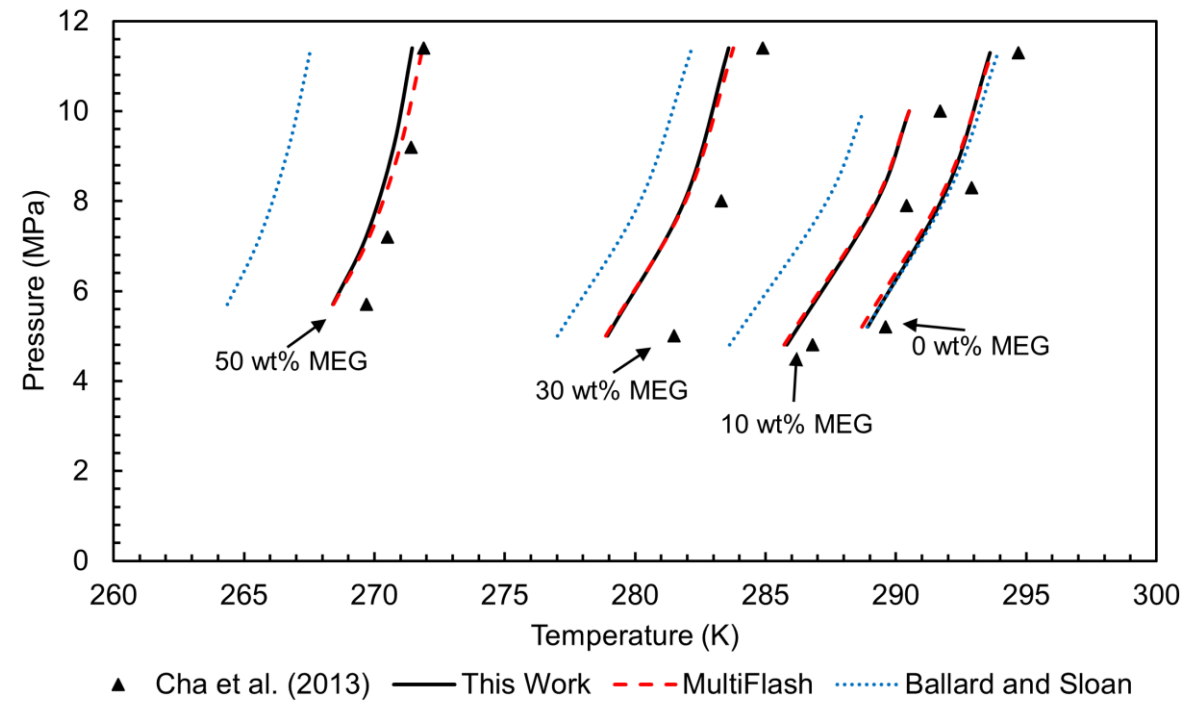


Figure S56: Experimental hydrate equilibrium data of a multicomponent gas mixture at different wt% of MEG, alongside predictions from the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Dataset:¹⁸⁸ - water-free molar composition: $0.9 \text{ CH}_4 + 0.06 \text{ C}_2\text{H}_6 + 0.03 \text{ C}_3\text{H}_8 + 0.01 \text{ n-C}_4\text{H}_{10}$

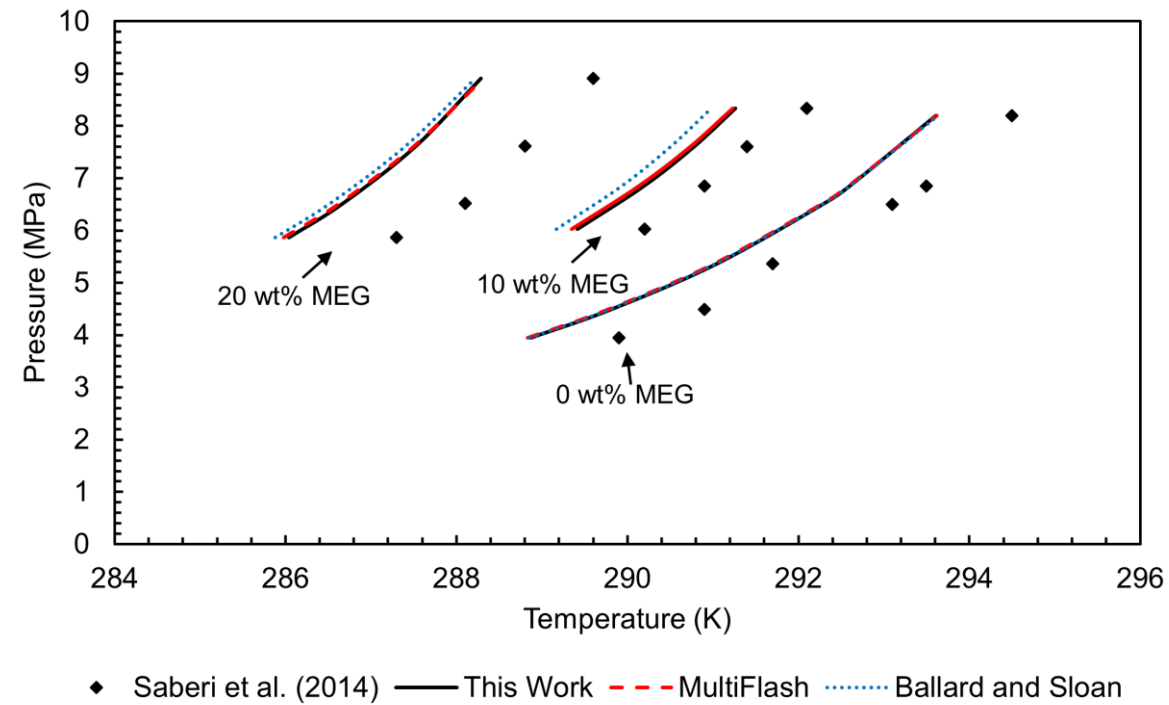


Figure S57: Experimental hydrate equilibrium data of a multicomponent gas mixture at different wt% of MEG, alongside predictions from the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Dataset:⁵¹ - water-free molar composition: $0.804 \text{ CH}_4 + 0.103 \text{ C}_2\text{H}_6 + 0.05 \text{ C}_3\text{H}_8 + 0.0165 \text{ i-C}_4\text{H}_{10} + 0.0072 \text{ n-C}_4\text{H}_{10} + 0.0011 \text{ N}_2 + 0.0182 \text{ CO}_2$

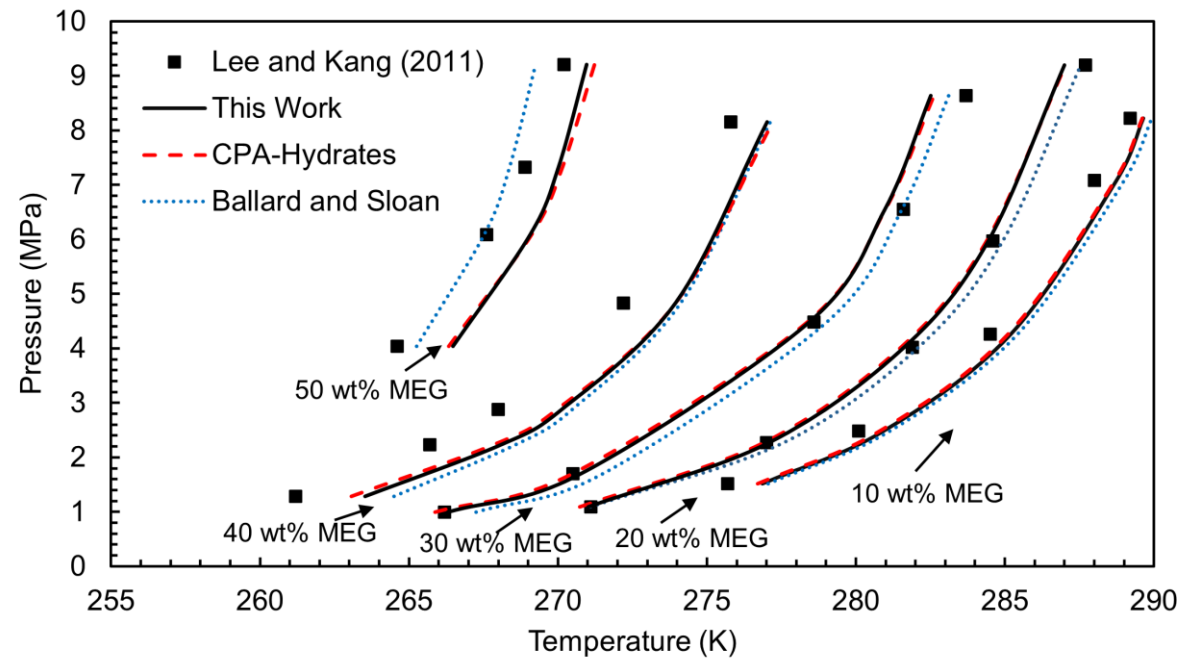


Figure S58: Experimental hydrate equilibrium data of a multicomponent gas mixture at different wt% of MEG, alongside predictions from the CaSH model (black), MultiFlash 7.0 CPA-Hydrates (red-dashed), and Ballard and Sloan (blue-dotted). Dataset:¹⁹⁰ - water-free molar composition: $0.8986 \text{ CH}_4 + 0.064 \text{ C}_2\text{H}_6 + 0.0271 \text{ C}_3\text{H}_8 + 0.0048 \text{ i-C}_4\text{H}_{10} + 0.0049 \text{ n-C}_4\text{H}_{10} + 0.0004 \text{ N}_2$

References

- 1 M. Michelsen and J. Mollerup, *Thermodynamic modelling: Fundamentals and computational aspects*, 2007.
- 2 G. M. Kontogeorgis and G. K. Folas, [*Thermodynamic models for industrial applications*](#), John Wiley & Sons, Ltd, Chichester, UK, 2010.
- 3 M. L. Michelsen and E. M. Hendriks, [*Physical properties from association models*](#), *Fluid Phase Equilibria*, 2001, **180**, 165–174.
- 4 A. L. Ballard, PhD Thesis, Colorado School of Mines, 2002.
- 5 A. L. Ballard and J. D. Sloan, [*The next generation of hydrate prediction: An overview*](#), *Journal of Supramolecular Chemistry*, 2002, **2**, 385–392.
- 6 S. Hielscher, PhD thesis, Fakultät für Maschinenbau der Ruhr-Universität Bochum, 2019.
- 7 S. Hielscher, B. Semrau, A. Jäger, V. Vinš, C. Bretkopf, J. Hrubý and R. Span, [*Modification of a model for mixed hydrates to represent double cage occupancy*](#), *Fluid Phase Equilibria*, 2019, **490**, 48–60.
- 8 S. Adisasmito, R. J. Frank and E. D. Sloan, [*Hydrates of carbon dioxide and methane mixtures*](#), *Journal of Chemical and Engineering Data*, 1991, **36**, 68–71.
- 9 M. Aghajanloo, Z. Taheri, T. J. Behbahani, A. H. Mohammadi, M. R. Ehsani and H. Heydarian, [*Experimental determination and thermodynamic modeling of clathrate hydrate stability conditions in methane + hydrogen sulfide + water system*](#), *Journal of Natural Gas Science and Engineering*, 2020, **83**, 103549.
- 10 C. Blanc and J. (Elf. A. (FR)). Tornier-Lasserve, Controlling hydrates in high-pressure flowlines, *World Oil*, 1990, **211**, 63 et seq.

- 11 A. Böttger, Á. P.-S. Kamps and G. Maurer, [An experimental investigation of the phase equilibrium of the binary system \(methane+water\) at low temperatures: Solubility of methane in water and three-phase \(vapour+liquid+hydrate\) equilibrium](#), *Fluid Phase Equilibria*, 2016, **407**, 209–216.
- 12 L. CHEN, C. SUN, G. CHEN, Y. NIE, Z. SUN and Y. LIU, [Measurements of hydrate equilibrium conditions for CH₄, CO₂, and CH₄ + C₂H₆ + C₃H₈ in various systems by step-heating method](#), *Chinese Journal of Chemical Engineering*, 2009, **17**, 635–641.
- 13 M. Clarke and P. R. Bishnoi, [Determination of the activation energy and intrinsic rate constant of methane gas hydrate decomposition](#), *Canadian Journal of Chemical Engineering*, 2001, **79**, 143–147.
- 14 D. É. S. de Menezes, P. de A. Pessôa Filho and M. D. Robustillo Fuentes, Phase equilibrium for methane, ethane and carbon dioxide hydrates at pressures up to 100 MPa through high-pressure microcalorimetry: Experimental data, analysis and modeling, *Fluid Phase Equilibria*, DOI:[10.1016/j.fluid.2020.112590](#).
- 15 J. L. De Roo, C. J. Peters, R. N. Lichtenthaler and G. A. M. Diepen, [Occurrence of methane hydrate in saturated and unsaturated solutions of sodium chloride and water in dependence of temperature and pressure](#), *AIChE Journal*, 1983, **29**, 651–657.
- 16 E. M. Frost Jr and W. M. Deaton, Gas hydrate composition and equilibrium data.[direct and calculated measurements are in close agreement; CO/sub 2/, CH/sub 4/, c/sub 2/h/sub 6/, c/sub 3/h/sub 8/used], *Oil Gas J.:(United States)*.
- 17 Y. Deng, X. Xu and L. Zhang, in *Permafrost sixth internaional conference*, Beijing, China, 1993.
- 18 G. R. Dickens and M. S. Quinby-Hunt, [Methane hydrate stability in seawater](#), *Geophysical Research Letters*, 1994, **21**, 2115–2118.
- 19 Yu. A. Dyadin and E. Y. Aladko, in *International conference on natural gas hydrates*, Toulouse, France, 1996, pp. 67–70.

- 20 T. J. Galloway, W. Ruska, P. S. Chappellear and R. Kobayashi, [Experimental measurement of hydrate numbers for methane and ethane and comparison with theoretical values](#), *Industrial and Engineering Chemistry Fundamentals*, 1970, **9**, 237–243.
- 21 P. Gayet, C. Dicharry, G. Marion, A. Graciaa, J. Lachaise and A. Nesterov, [Experimental determination of methane hydrate dissociation curve up to 55MPa by using a small amount of surfactant as hydrate promoter](#), *Chemical Engineering Science*, 2005, **60**, 5751–5758.
- 22 R. L. Guo, G. B., Bretz, R. E., Lee and R. L. Guo, G. B., Bretz, R.E., Lee, in *International gas research conference*, Orlando, Florida, 1992, pp. 231–240.
- 23 A. Hachikubo, A. Miyamoto, K. Hyakutake, K. Abe and H. Shoji, in *Fourth international conference on gas hydrates, japan*, 2002, pp. 357–360.
- 24 Y. Hu, T. Y. Makogon, P. Karanjkar, K.-H. H. Lee, B. R. Lee, A. K. Sum, T. Y. Makogon, P. Karanjkar, K.-H. H. Lee, B. R. Lee and A. K. Sum, [Gas hydrates phase equilibria and formation from high concentration NaCl brines up to 200 MPa](#), *Journal of Chemical and Engineering Data*, 2017, **62**, 1910–1918.
- 25 Y. Hu, B. R. Lee and A. K. Sum, [Universal correlation for gas hydrates suppression temperature of inhibited systems: I. Single salts](#), *AIChE Journal*, 2017, **63**, 5111–5124.
- 26 U. Hütz and P. Englezos, Measurement of structure h hydrate phase equilibrium and the effect of electrolytes, *Fluid Phase Equilibria*, 1996, **117**, 178–185.
- 27 M. D. Jager, PhD thesis, Colarado School of Mines, 2001.
- 28 M. D. Jager and E. D. Sloan, [The effect of pressure on methane hydration in pure water and sodium chloride solutions](#), *Fluid Phase Equilibria*, 2001, **185**, 89–99.

- 29 J. Javanmardi, S. Babae, A. Eslamimanesh and A. H. Mohammadi, [Experimental measurements and predictions of gas hydrate dissociation conditions in the presence of methanol and ethane-1,2-diol aqueous solutions](#), *Journal of Chemical and Engineering Data*, 2012, **57**, 1474–1479.
- 30 J. Jhaveri and D. B. Robinson, [Hydrates in the methane-nitrogen system](#), *The Canadian Journal of Chemical Engineering*, 1965, **43**, 75–78.
- 31 A. Kamari, H. Hashemi, S. Babae, A. H. Mohammadi and D. Ramjugernath, [Phase stability conditions of carbon dioxide and methane clathrate hydrates in the presence of KBr, CaBr₂, MgCl₂, HCOONa, and HCOOK aqueous solutions: Experimental measurements and thermodynamic modelling](#), *Journal of Chemical Thermodynamics*, 2017, **115**, 307–317.
- 32 M. Kharrat and D. Dalmazzone, [Experimental determination of stability conditions of methane hydrate in aqueous calcium chloride solutions using high pressure differential scanning calorimetry](#), *Journal of Chemical Thermodynamics*, 2003, **35**, 1489–1505.
- 33 R. Kobayashi and D. L. Katz, Methane hydrate at high pressure, *Journal of Petroleum Technology*, 1949, **1**, 66–70.
- 34 T. Komai, Y. Yamamoto and S. Ikegami, in *Fuel chemistry symposium on gas hydrates*, American Chemical Society, San Francisco, CA, USA, 1997, pp. 568–572.
- 35 P. G. Lafond, K. A. Olcott, E. Dendy Sloan, C. A. Koh and A. K. Sum, [Measurements of methane hydrate equilibrium in systems inhibited with NaCl and methanol](#), *Journal of Chemical Thermodynamics*, 2012, **48**, 1–6.
- 36 D. Lim, H. Ro, Y. Seo, Y. ju Seo, J. Y. Lee, S. J. Kim, J. Lee and H. Lee, [Thermodynamic stability and guest distribution of CH₄/N₂/CO₂ mixed hydrates for methane hydrate production using N₂/CO₂ injection](#), *Journal of Chemical Thermodynamics*, 2017, **106**, 16–21.

- 37 T. Maekawa, [Equilibrium conditions for gas hydrates of methane and ethane mixtures in pure water and sodium chloride solution](#), *Geochemical Journal*, 2001, **35**, 59–66.
- 38 T. Maekawa, [Equilibrium conditions for clathrate hydrates formed from methane and aqueous propanol solutions](#), *Fluid Phase Equilibria*, 2008, **267**, 1–5.
- 39 D. R. Marshall, S. Saito and R. Kobayashi, [Hydrates at high pressures: Part i. Methane-water, argon-water, and nitrogen-water systems](#), *AIChE Journal*, 1964, **10**, 202–205.
- 40 H. O. McLeod and J. M. Campbell, [Natural gas hydrates at pressures to 10,000 psia](#), *Journal of Petroleum Technology*, 1961, **13**, 590–594.
- 41 A. H. Mohammadi, B. Tohidi and R. W. Burgass, [Equilibrium data and thermodynamic modeling of nitrogen, oxygen, and air clathrate hydrates](#), *Journal of Chemical & Engineering Data*, 2003, **48**, 612–616.
- 42 A. H. Mohammadi, R. Anderson and B. Tohidi, Carbon monoxide clathrate hydrates: Equilibrium data and thermodynamic modeling, *AIChE journal*, 2005, **51**, 2825–2833.
- 43 L. Mu and N. von Solms, [Hydrate thermal dissociation behavior and dissociation enthalpies in methane-carbon dioxide swapping process](#), *Journal of Chemical Thermodynamics*, 2018, **117**, 33–42.
- 44 T. Nakamura, T. Makino, T. Sugahara and K. Ohgaki, Stability boundaries of gas hydrates helped by methane—structure-h hydrates of methylcyclohexane and cis-1, 2-dimethylcyclohexane, *Chemical engineering science*, 2003, **58**, 269–273.
- 45 S. Nakano, M. Moritoki and K. Ohgaki, [High-pressure phase equilibrium and raman microprobe spectroscopic studies on the methane hydrate system](#), *Journal of Chemical and Engineering Data*, 1999, **44**, 254–257.

- 46 J. Nixdorf and L. R. Oellrich, [Experimental determination of hydrate equilibrium conditions for pure gases, binary and ternary mixtures and natural gases](#), *Fluid Phase Equilibria*, 1997, **139**, 325–333.
- 47 K. Ohgaki, K. Takano, H. Sangawa, T. Matsubara and S. Nakano, [Methane exploitation by carbon dioxide from gas hydrates. Phase equilibria for CO₂-CH₄ mixed hydrate system.](#), *JOURNAL OF CHEMICAL ENGINEERING OF JAPAN*, 1996, **29**, 478–483.
- 48 R. Ohmura, S. Kashiwazaki, S. Shiota, H. Tsuji and Y. H. Mori, [Structure-i and structure-h hydrate formation using water spraying](#), *Energy & Fuels*, 2002, **16**, 1141–1147.
- 49 H. Pahlavanzadeh, H. Hassan and M. Pourranjbar, [Hydrate dissociation conditions of CH₄ in the presence of TBANO₃ and cyclopentane promoter mixture: Thermodynamic modeling and experimental measurement](#), *Journal of Chemical and Engineering Data*, 2020, **65**, 1927–1935.
- 50 O. L. Roberts, E. R. Brownscombe, L. S. Howe and H. Ramser, Constitution diagrams and composition of methane and ethane hydrates, *Oil Gas J*, 1940, **39**, 37–43.
- 51 A. Saberi, A. Alamdari, A. Shariati and A. H. Mohammadi, [Experimental measurement and thermodynamic modeling of equilibrium condition for natural gas hydrate in MEG aqueous solution](#), *Fluid Phase Equilibria*, 2018, **459**, 110–118.
- 52 K. M. Sabil, Q. Nasir, B. Partoon and A. A. Seman, [Measurement of h-LW-v and dissociation enthalpy of carbon dioxide rich synthetic natural gas mixtures](#), *Journal of Chemical & Engineering Data*, 2014, **59**, 3502–3509.
- 53 D. Sadeq, S. Iglauer, M. Lebedev, C. Smith and A. Barifcani, [Experimental determination of hydrate phase equilibrium for different gas mixtures containing methane, carbon dioxide and nitrogen with motor current measurements](#), *Journal of Natural Gas Science and Engineering*, 2017, **38**, 59–73.
- 54 N. A. Sami, K. Das, J. S. Sangwai and N. Balasubramanian, [Phase equilibria of methane and carbon dioxide clathrate hydrates in the presence of \(methanol+MgCl₂\) and \(ethylene glycol+MgCl₂\) aqueous solutions](#), *The Journal of Chemical Thermodynamics*, 2013, **65**, 198–203.

- 55 P. Servio and P. Englezos, [Measurement of dissolved methane in water in equilibrium with its hydrate](#), *Journal of Chemical & Engineering Data*, 2002, **47**, 87–90.
- 56 E. A. Smelik and H. E. King, [Crystal-growth studies of natural gas clathrate hydrates using a pressurized optical cell](#), *American Mineralogist*, 1997, **82**, 88–98.
- 57 S. Sun, J. Zhao and D. Yu, [Dissociation enthalpy of methane hydrate in salt solution](#), *Fluid Phase Equilibria*, 2018, **456**, 92–97.
- 58 T. M. Svartas and E. H. Fadnes, in *Proceedings of the second (1992) international offshore and polar engineering conference*, 1992, vol. I, pp. 614–619.
- 59 J. L. Thakore and G. D. Holder, [Solid—vapor azeotropes in hydrate-forming systems](#), *Industrial and Engineering Chemistry Research*, 1987, **26**, 462–469.
- 60 D. L. Verma, Y. K., Hand, J. H., Katz, in *GVC/AIChE join meeting at munich, 1975*, 1974.
- 61 Z. T. Ward, C. E. Deering, R. A. Marriott, A. K. Sum, E. D. Sloan and C. A. Koh, [Phase equilibrium data and model comparisons for H₂S hydrates](#), *Journal of Chemical & Engineering Data*, 2015, **60**, 403–408.
- 62 K. Xiao, C. Zou, Y. Yang, H. Zhang, H. Li and Z. Qin, [A preliminary study of the gas hydrate stability zone in a gas hydrate potential region of china](#), *Energy Science and Engineering*, 2019, **8**, 1080–1091.
- 63 S. Xu, S. Fan, H. Yao, Y. Wang, X. Lang, P. Lv and S. Fang, [The phase equilibria of multicomponent gas hydrate in methanol/ethylene glycol solution based formation water](#), *The Journal of Chemical Thermodynamics*, 2017, **104**, 212–217.
- 64 S. O. Yang, S. H. Cho, H. Lee and C. S. Lee, [Measurement and prediction of phase equilibria for water + methane in hydrate forming conditions](#), *Fluid Phase Equilibria*, 2001, **185**, 53–63.

- 65 K. Yasuda and R. Ohmura, [Phase equilibrium for clathrate hydrates formed with methane, ethane, propane, or carbon dioxide at temperatures below the freezing point of water](#), *Journal of Chemical & Engineering Data*, 2008, **53**, 2182–2188.
- 66 T. Y. Makogon and E. D. Sloan, [Phase equilibrium for methane hydrate from 190 to 262 k](#), *Journal of Chemical and Engineering Data*, 1994, **39**, 351–353.
- 67 H. D. Nagashima, N. Fukushima and R. Ohmura, [Phase equilibrium condition measurements in carbon dioxide clathrate hydrate forming system from 199.1 k to 247.1 k](#), *Fluid Phase Equilibria*, 2016, **413**, 53–56.
- 68 D. A. Avlonitis, Master of Science Thesis, Heriot-Watt University, 1988.
- 69 P. Englezos and P. R. Bishnoi, [Experimental study on the equilibrium ethane hydrate formation conditions in aqueous electrolyte solutions](#), *Industrial and Engineering Chemistry Research*, 1991, **30**, 1655–1659.
- 70 B. J. Falabella and M. Vanpee, Experimental determination of gas hydrate equilibrium below the ice point, 1974, **13**, 1–4.
- 71 S. Hashimoto, A. Sasatani, Y. Matsui, T. Sugahara and K. Ohgaki, [Isothermal phase equilibria for methane + ethane + water ternary system containing gas hydrates](#), *The Open Thermodynamics Journal*, 2008, **2**, 100–105.
- 72 G. D. Holder and G. C. Grigoriou, [Hydrate dissociation pressures of \(methane + ethane + water\) existence of a locus of minimum pressures](#), *Journal of Chemical Thermodynamics*, 1980, **12**, 1093–1104.
- 73 G. D. Holder and S. P. Godbole, [Measurement and prediction of dissociation pressures of isobutane and propane hydrates below the ice point](#), *AIChE Journal*, 1982, **28**, 930–934.
- 74 Z. Long, J.-W. Du, D. Li and D. Liang, [Phase equilibria of ethane hydrate in MgCl₂ aqueous solutions](#), *Journal of Chemical & Engineering Data*, 2010, **55**, 2938–2941.

- 75 T. Maekawa, [Equilibrium conditions of ethane hydrates in the presence of aqueous solutions of alcohols, glycols, and glycerol](#), *Journal of Chemical & Engineering Data*, 2012, **57**, 526–531.
- 76 Y. Matsui, Y. Ogura, H. Miyauchi, T. Makino, T. Sugahara and K. Ohgaki, [Isothermal phase equilibria for binary hydrate systems of carbon dioxide + ethane and carbon dioxide + tetrafluoromethane](#), *Journal of Chemical and Engineering Data*, 2010, **55**, 3297–3301.
- 77 A. H. Mohammadi and D. Richon, [Ice-clathrate hydrate-gas phase equilibria for air, oxygen, nitrogen, carbon monoxide, methane, or ethane + water system](#), *Industrial & Engineering Chemistry Research*, 2010, **49**, 3976–3979.
- 78 A. H. Mohammadi, W. Afzal and D. Richon, [Experimental data and predictions of dissociation conditions for ethane and propane simple hydrates in the presence of distilled water and methane, ethane, propane, and carbon dioxide simple hydrates in the presence of ethanol aqueous solutions](#), *Journal of Chemical & Engineering Data*, 2008, **53**, 73–76.
- 79 K. Morita, S. Nakano and K. Ohgaki, [Structure and stability of ethane hydrate crystal](#), *Fluid Phase Equilibria*, 2000, **169**, 167–175.
- 80 S. Nakano, K. Yamamoto and K. Ohgaki, [Natural gas exploitation by carbon dioxide from gas hydrate fields - high-pressure phase equilibrium for an ethane hydrate system](#), *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 1998, **212**, 159–163.
- 81 H.-J. Ng, C.-J. Chen and D. B. Robinson, *The effect of ethylene glycol or methanol on hydrate formation in systems containing ethane, propane, carbon dioxide, hydrogen sulfide, or a typical gas condensate*, Gas Processors Association, 1985.
- 82 H. J. Ng and D. B. Robinson, Equilibrium phase composition and hydrating conditions in systems containing methanol, light hydrocarbons, carbon dioxide, and hydrogen sulfide, *Gas Processors Association - Research Report*.
- 83 H. H. Reamer, F. T. Selleck and B. H. Sage, [Some properties of mixed paraffinic and olefinic hydrates](#), *Journal of Petroleum Technology*, 1952, **4**, 197–202.

- 84 J. M. Chima-Maceda, P. Esquivel-Mora, A. Pimentel-Rodas, L. A. Galicia-Luna and J. J. Castro-Arellano, [Effect of 1-propanol and TBAB on gas hydrates dissociation conditions for CO₂ + hexane + water systems](#), *Journal of Chemical & Engineering Data*, 2019, **64**, 4775–4780.
- 85 M. L. Dai, Z. G. Sun, J. Li, C. M. Li and H. F. Huang, [Effect of n-dodecane on equilibrium dissociation conditions of carbon dioxide hydrate](#), *Journal of Chemical Thermodynamics*, 2020, **148**, 106144.
- 86 P. D. Dholabhai, N. Kalogerakis and P. R. Bishnoi, [Equilibrium conditions for carbon dioxide hydrate formation in aqueous electrolyte solutions](#), *Journal of Chemical and Engineering Data*, 1993, **38**, 650–654.
- 87 S.-S. Fan and T.-M. Guo, [Hydrate formation of CO₂-rich binary and quaternary gas mixtures in aqueous sodium chloride solutions](#), *Journal of Chemical & Engineering Data*, 1999, **44**, 829–832.
- 88 S. S. Fan, G. J. Chen, Q. L. Ma and T. M. Guo, [Experimental and modeling studies on the hydrate formation of CO₂ and CO₂-rich gas mixtures](#), *Chemical Engineering Journal*, 2000, **78**, 173–178.
- 89 P. F. Ferrari, A. Z. Guembaroski, M. A. M. Neto, R. E. M. M. Morales, A. K. Sum, M. A. Marcelino Neto, R. E. M. M. Morales and A. K. Sum, [Experimental measurements and modelling of carbon dioxide hydrate phase equilibrium with and without ethanol](#), *Fluid Phase Equilibria*, 2016, **413**, 176–183.
- 90 P. Ilani-Kashkouli, A. H. Mohammadi, P. Naidoo and D. Ramjugernath, [Thermodynamic stability conditions for semi-clathrate hydrates of CO₂, CH₄, or N₂ with tetrabutyl ammonium nitrate \(TBANO₃\) aqueous solution](#), *The Journal of Chemical Thermodynamics*, 2016, **96**, 52–56.
- 91 A. Jarrahan and A. Nakhaee, [Hydrate–liquid–vapor equilibrium condition of N₂+ CO₂ + H₂O system: Measurement and modeling](#), *Fuel*, 2019, **237**, 769–774.

- 92 M. S. Khan, B. Partoon, C. B. Bavoh, B. Lal and N. B. Mellon, [Influence of tetramethylammonium hydroxide on methane and carbon dioxide gas hydrate phase equilibrium conditions](#), *Fluid Phase Equilibria*, 2017, **440**, 1–8.
- 93 S. D. Larson, *PHASE STUDIES OF THE TWO-COMPONENT CARBON-DIOXIDE-WATER SYSTEM INVOLVING THE CARBON-DIOXIDE HYDRATE*, University of Illinois at Urbana-Champaign, 1955.
- 94 Y. Lee, T. Kawamura, Y. Yamamoto and J. Yoon, [Phase equilibrium studies of tetrahydrofuran \(THF\) + CH₄, THF + CO₂, CH₄ + CO₂, and THF + CO₂ + CH₄ hydrates](#), *Journal of Chemical & Engineering Data*, 2012, **57**, 3543–3548.
- 95 T. Maekawa, [Equilibrium conditions for carbon dioxide hydrates in the presence of aqueous solutions of alcohols, glycols, and glycerol](#), *Journal of Chemical & Engineering Data*, 2010, **55**, 1280–1284.
- 96 N. Mannar, C. B. Bavoh, A. H. Baharudin, B. Lal and N. B. Mellon, [Thermophysical properties of aqueous lysine and its inhibition influence on methane and carbon dioxide hydrate phase boundary condition](#), *Fluid Phase Equilibria*, 2017, **454**, 57–63.
- 97 V. P. Melnikov, A. N. Nesterov, A. M. Reshetnikov and V. A. Istomin, [Metastable states during dissociation of carbon dioxide hydrates below 273K](#), *Chemical Engineering Science*, 2011, **66**, 73–77.
- 98 A. H. Mohammadi, Phase stability conditions of carbon dioxide clathrate hydrate in the presence of ethanol and ethanol + salt aqueous solutions, *Petroleum and Coal*, 2018, **60**, 349–352.
- 99 A. H. Mohammadi and D. Richon, [Ice-clathrate hydrate-gas phase equilibria for argon + water and carbon dioxide + water systems](#), *Industrial and Engineering Chemistry Research*, 2011, **50**, 11452–11454.
- 100 Y. Nema, R. Ohmura, I. Senaha and K. Yasuda, [Quadruple point determination in carbon dioxide hydrate forming system](#), *Fluid Phase Equilibria*, 2017, **441**, 49–53.

- 101 K. Ohgaki, Y. Makihara and K. Takano, [Formation of CO₂ hydrate in pure and sea waters.](#), *JOURNAL OF CHEMICAL ENGINEERING OF JAPAN*, 1993, **26**, 558–564.
- 102 D. B. Robinson and B. R. Metha, Hydrates in the PropaneCarbon dioxide- water system, *Journal of Canadian Petroleum Technology*, DOI:[10.2118/71-01-04](#).
- 103 L. Ruffine and J. P. M. Trusler, [Phase behaviour of mixed-gas hydrate systems containing carbon dioxide](#), *Journal of Chemical Thermodynamics*, 2010, **42**, 605–611.
- 104 K. M. Sabil, G. J. Witkamp and C. J. Peters, [Estimations of enthalpies of dissociation of simple and mixed carbon dioxide hydrates from phase equilibrium data](#), *Fluid Phase Equilibria*, 2010, **290**, 109–114.
- 105 M. Seif, A. Kamran-Pirzaman and A. H. Mohammadi, [Phase equilibria of clathrate hydrates in CO₂/CH₄ + \(1-propanol/2-propanol\) + water systems: Experimental measurements and thermodynamic modeling](#), *The Journal of Chemical Thermodynamics*, 2018, **118**, 58–66.
- 106 Y.-T. Seo, S.-P. Kang, H. Lee, C.-S. Lee and W.-M. Sung, [Hydrate phase equilibria for gas mixtures containing carbon dioxide: A proof-of-concept to carbon dioxide recovery from multicomponent gas stream](#), *Korean Journal of Chemical Engineering*, 2000, **17**, 659–667.
- 107 P. Servio and P. Englezos, [Effect of temperature and pressure on the solubility of carbon dioxide in water in the presence of gas hydrate](#), *Fluid Phase Equilibria*, 2001, **190**, 127–134.
- 108 D. Sun, J. Ripmeester and P. Englezos, [Phase equilibria for the CO₂/CH₄/N₂/H₂O system in the hydrate region under conditions relevant to storage of CO₂ in depleted natural gas reservoirs](#), *Journal of Chemical and Engineering Data*, 2016, **61**, 4061–4067.
- 109 S. Takenouchi and G. C. Kennedy, Dissociation pressures of the phase CO₂ 3/4 H₂O, *The Journal of geology*, 1965, **73**, 383–390.
- 110 C. H. Unruh and D. L. Katz, [Gas hydrates of carbon dioxide-methane mixtures](#), *Journal of Petroleum Technology*, 1949, **1**, 83–86.

- 111 J. G. Vlahakis, The growth rate of ice crystals: The properties of carbon dioxide hydrate a review of properties of 51 gas hydrates, *OSW*, 1972, **830**, 36.
- 112 M. Wendland, H. Hasse and G. Maurer, [Experimental pressure-temperature data on three- and four-phase equilibria of fluid, hydrate, and ice phases in the system carbon dioxide-water](#), *Journal of Chemical and Engineering Data*, 1999, **44**, 901–906.
- 113 J.-H. Yoon and H. Lee, [Clathrate phase equilibria for the water–phenol–carbon dioxide system](#), *AIChE Journal*, 1997, **43**, 1884–1893.
- 114 Y. S. Yu, S. D. Zhou, X. S. Li and S. L. Wang, [Effect of graphite nanoparticles on CO₂ hydrate phase equilibrium](#), *Fluid Phase Equilibria*, 2016, **414**, 23–28.
- 115 L. Zha, D. Q. Liang and D. L. Li, [Phase equilibria of CO₂ hydrate in NaCl-MgCl₂ aqueous solutions](#), *Journal of Chemical Thermodynamics*, 2012, **55**, 110–114.
- 116 H. KUBOTA, K. SHIMIZU, Y. TANAKA and T. MAKITA, [Thermodynamic properties of R13 \(CClF₃\), R23 \(CHF₃\), R152a \(C₂H₄F₂\), and propane hydrates for desalination of sea water.](#), *JOURNAL OF CHEMICAL ENGINEERING OF JAPAN*, 1984, **17**, 423–429.
- 117 T. Maekawa, [Equilibrium conditions of propane hydrates in aqueous solutions of alcohols, glycols, and glycerol](#), *Journal of Chemical and Engineering Data*, 2008, **53**, 2838–2843.
- 118 M. M. M. V. Den Heuvel, C. J. Peters and J. De Swaan Arons, [Gas hydrate phase equilibria for propane in the presence of additive components](#), *Fluid Phase Equilibria*, 2002, **193**, 245–259.
- 119 S. L. Patil, M.Sc. thesis, University of Alaska, Anchorage, Alaska, USA, 1987.
- 120 Y. Lee, S. Lee, J. Lee and Y. Seo, [Structure identification and dissociation enthalpy measurements of the CO₂+N₂ hydrates for their application to CO₂ capture and storage](#), *Chemical Engineering Journal*, 2014, **246**, 20–26.

- 121 K. Sugahara, Y. Tanaka, T. Sugahara and K. Ohgaki, [Thermodynamic stability and structure of nitrogen hydrate crystal](#), *Journal of Supramolecular Chemistry*, 2002, **2**, 365–368.
- 122 A. van Cleeff and G. A. M. Diepen, [Gas hydrates of nitrogen and oxygen](#), *Recueil des Travaux Chimiques des Pays-Bas*, 2010, **79**, 582–586.
- 123 K. Yasuda, Y. Oto, R. Shen, T. Uchida and R. Ohmura, [Phase equilibrium condition measurements in nitrogen and air clathrate hydrate forming systems at temperatures below freezing point of water](#), *Journal of Chemical Thermodynamics*, 2013, **67**, 143–147.
- 124 K. I. Adeniyi, C. E. Deering, G. P. Nagabhushana and R. A. Marriott, [Hydrogen sulfide hydrate dissociation in the presence of liquid water](#), *Industrial and Engineering Chemistry Research*, 2018, **57**, 15579–15585.
- 125 D. C. Bond and N. B. Russell, [Effect of antifreeze agents on the formation of hydrogen sulphide hydrate](#), *Transactions of the AIME*, 1949, **179**, 192–198.
- 126 J. J. Carroll and A. E. Mather, [Phase equilibrium in the system water-hydrogen sulphide: Hydrate-forming conditions](#), *The Canadian Journal of Chemical Engineering*, 1991, **69**, 1206–1212.
- 127 K. N. Mahadev and P. R. Bishnoi, [Equilibrium conditions for the hydrogen sulfide hydrate formation in the presence of electrolytes and methanol](#), *Canadian Journal of Chemical Engineering*, 1999, **77**, 718–722.
- 128 A. H. Mohammadi and D. Richon, [Equilibrium data of methyl cyclohexane + hydrogen sulfide and methyl cyclohexane + methane clathrate hydrates](#), *Journal of Chemical & Engineering Data*, 2009, **55**, 566–569.
- 129 F. T. Selleck, L. T. Carmichael and B. H. Sage, [Phase behavior in the hydrogen sulfide-water system](#), *Industrial & Engineering Chemistry*, 1952, **44**, 2219–2226.

- 130 A. H. Mohammadi and D. Richon, [Methane hydrate phase equilibrium in the presence of salt \(NaCl, KCl, or CaCl₂\) + ethylene glycol or salt \(NaCl, KCl, or CaCl₂\) + methanol aqueous solution: Experimental determination of dissociation condition](#), *Journal of Chemical Thermodynamics*, 2009, **41**, 1374–1377.
- 131 O. S. Rouher and A. J. Barduhn, [Hydrates of iso- and normal butane and their mixtures](#), *Desalination*, 1969, **6**, 57–73.
- 132 G. R. Schneider and J. Farrar, *Nucleation and growth of ice crystals*, US Department of the Interior USA, 1968.
- 133 B.-J. Wu, D. B. Robinson and H.-J. Ng, [Three- and four-phase hydrate forming conditions in methane + isobutane + water](#), *The Journal of Chemical Thermodynamics*, 1976, **8**, 461–469.
- 134 P. V. Hemmingsen, R. Burgass, K. S. Pedersen, K. Kinnari and H. Sørensen, [Hydrate temperature depression of MEG solutions at concentrations up to 60wt%. Experimental data and simulation results](#), *Fluid Phase Equilibria*, 2011, **307**, 175–179.
- 135 S. Ovalle and J. G. Beltran, [Growth mechanisms and phase equilibria of propane and methane + propane hydrates](#), *Journal of Chemical & Engineering Data*, 2021, acs.jced.1c00329.
- 136 S. G. Paranjpe, S. L. Patil, V. A. Kamath and S. P. Godbole, in *SPE annual technical conference and exhibition*, 1987, pp. 379–390.
- 137 C. Smith, D. Pack and A. Barifcani, [Propane, n-butane and i-butane stabilization effects on methane gas hydrates](#), *The Journal of Chemical Thermodynamics*, 2017, **115**, 293–301.
- 138 H. Bruusgaard, A. Carbone and P. Servio, [H–l w –v equilibrium measurements for the CH₄ + c₂h₆ + h₂o hydrate forming system](#), *Journal of Chemical & Engineering Data*, 2010, **55**, 3680–3683.
- 139 Y. Hu, T. Y. Makogon, P. Karanjkar, K. H. Lee, B. R. Lee and A. K. Sum, [Gas hydrates phase equilibria for structure I and II hydrates with chloride salts at high salt concentrations and up to 200 MPa](#), *Journal of Chemical Thermodynamics*, 2018, **117**, 27–32.

- 140 S. Subramanian, R. A. Kini, S. F. Dec and E. D. Sloan, [Evidence of structure II hydrate formation from methane+ethane mixtures](#), *Chemical Engineering Science*, 2000, **55**, 1981–1999.
- 141 H. Bruusgaard, J. G. Beltrán and P. Servio, [Vapor-liquid water-hydrate equilibrium data for the system N₂ + CO₂ + H₂O](#), *Journal of Chemical and Engineering Data*, 2008, **53**, 2594–2597.
- 142 G. DOYNE, PhD thesis, University of Michigan, 1976.
- 143 M. M. den Heuvel, Phase behaviour and structural aspects of ternary clathrate hydrate systems: The role of additives, *Technische Universiteit Delft, Netherlands*.
- 144 V. Belandria, A. H. Mohammadi and D. Richon, [Phase equilibria of clathrate hydrates of methane+carbon dioxide: New experimental data and predictions](#), *Fluid Phase Equilibria*, 2010, **296**, 60–65.
- 145 V. Belandria, A. Eslamimanesh, A. H. Mohammadi, P. Théveneau, H. Legendre and D. Richon, [Compositional analysis and hydrate dissociation conditions measurements for carbon dioxide + methane + water system](#), *Industrial and Engineering Chemistry Research*, 2011, **50**, 5783–5794.
- 146 V. R. Belosludov, Y. Y. Bozhko, O. S. Subbotin, R. V. Belosludov, R. K. Zhdanov, K. V. Gets and Y. Kawazoe, [Influence of N₂ on formation conditions and guest distribution of mixed CO₂ + CH₄ gas hydrates](#), *Molecules*, 2018, **23**, 1–15.
- 147 J. G. Beltrán and P. Servio, [Equilibrium studies for the system methane+ carbon dioxide+ neohexane+ water](#), *Journal of Chemical & Engineering Data*, 2008, **53**, 1745–1749.
- 148 A. Chapoy, R. Burgass, B. Tohidi and I. Alsiyabi, [Hydrate and phase behavior modeling in CO₂-rich pipelines](#), *Journal of Chemical and Engineering Data*, 2015, **60**, 447–463.

- 149 S. Fan, S. You, Y. Wang, X. Lang, C. Yu, S. Wang, Z. Li, W. Li, Y. Liu and Z. Zhou, [Hydrate phase equilibrium of CH₄-rich binary and ternary gas mixtures in the presence of tetra-n-butyl ammonium bromide](#), *Journal of Chemical and Engineering Data*, 2019, **64**, 5929–5934.
- 150 J. M. Herri, A. Bouchemoua, M. Kwaterski, A. Fezoua, Y. Ouabbas and A. Cameirao, [Gas hydrate equilibria for CO₂-N₂ and CO₂-CH₄ gas mixtures-experimental studies and thermodynamic modelling](#), *Fluid Phase Equilibria*, 2011, **301**, 171–190.
- 151 P. Kastanidis, G. E. Romanos, A. K. Stubos, I. G. Economou and I. N. Tsimpanogiannis, [Two- and three-phase equilibrium experimental measurements for the ternary CH₄ + CO₂ + H₂O mixture](#), *Fluid Phase Equilibria*, 2017, **451**, 96–105.
- 152 M. S. Khan, B. Lal, A. M. Shariff and H. Mukhtar, [Ammonium hydroxide ILs as dual-functional gas hydrate inhibitors for binary mixed gas \(carbon dioxide and methane\) hydrates](#), *Journal of Molecular Liquids*, 2019, **274**, 33–44.
- 153 D. Le Quang, D. Le Quang, B. Bouillot, J.-M. Herri, P. Glenat and P. Duchet-Suchaux, [Experimental procedure and results to measure the composition of gas hydrate, during crystallization and at equilibrium, from n 2 –CO 2 –CH 4 –c 2 h 6 –c 3 h 8 –c 4 h 10 gas mixtures](#), *Fluid Phase Equilibria*, 2016, **413**, 10–21.
- 154 L. N. Legoix, L. Ruffine, C. Deusner and M. Haeckel, Experimental study of mixed gas hydrates from gas feed containing CH₄, CO₂ and N₂: Phase equilibrium in the presence of excess water and gas exchange, *Energies*, DOI:[10.3390/en11081984](#).
- 155 E. O. Obanijesu, A. Barifcani, V. K. Pareek and M. O. Tade, [Experimental study on feasibility of H₂ and N₂ as hydrate inhibitors in natural gas pipelines](#), *Journal of Chemical and Engineering Data*, 2014, **59**, 3756–3766.
- 156 B. Partoon, K. M. Sabil, H. Roslan, B. Lal and L. K. Keong, [Impact of acetone on phase boundary of methane and carbon dioxide mixed hydrates](#), *Fluid Phase Equilibria*, 2016, **412**, 51–56.
- 157 P. Servio, F. Lagers, C. Peters and P. Englezos, [Gas hydrate phase equilibrium in the system methane-carbon dioxide-neohexane and water](#), *Fluid Phase Equilibria*, 1999, **158-160**, 795–800.

- 158 L.-L. Shi, D.-Q. Liang and D.-L. Li, [Phase equilibrium conditions for simulated landfill gas hydrate formation in aqueous solutions of tetrabutylammonium nitrate](#), *The Journal of Chemical Thermodynamics*, 2014, **68**, 322–326.
- 159 X. Zang and D. Liang, [Phase equilibrium data for semiclathrate hydrate of synthesized binary CO₂/CH₄ gas mixture in tetra-n-butylammonium bromide aqueous solution](#), *Journal of Chemical and Engineering Data*, 2017, **62**, 851–856.
- 160 Y. D. Zhang, D. Wang, J. P. Yang, L. Tian and L. Wu, [Research on the hydrate formation in the process of gas phase CO₂ pipeline transportation](#), *International Journal of Heat and Technology*, 2016, **34**, 339–344.
- 161 S. Adisasmito and E. D. Sloan, [Hydrates of hydrocarbon gases containing carbon dioxide](#), *Journal of Chemical & Engineering Data*, 1992, **37**, 343–349.
- 162 H.-J. Ng and D. B. Robinson, [The measurement and prediction of hydrate formation in liquid hydrocarbon-water systems](#), *Industrial & Engineering Chemistry Fundamentals*, 1976, **15**, 293–298.
- 163 J.-W. Lee, D.-Y. Kim and H. Lee, [Phase behavior and structure transition of the mixed methane and nitrogen hydrates](#), *Korean Journal of Chemical Engineering*, 2006, **23**, 299–302.
- 164 D. H. Mei, J. Liao, J. T. Yang and T. M. Guo, [Experimental and modeling studies on the hydrate formation of a methane + nitrogen gas mixture in the presence of aqueous electrolyte solutions](#), *Industrial and Engineering Chemistry Research*, 1996, **35**, 4342–4347.
- 165 H.-J. Ng, J. P. Petrunia and D. B. Robinson, [Experimental measurement and prediction of hydrate forming conditions in the nitrogen-propane-water system](#), *Fluid Phase Equilibria*, 1977, **1**, 283–291.
- 166 V. Belandria, A. Eslamimanesh, A. H. Mohammadi and D. Richon, [Gas hydrate formation in carbon dioxide + nitrogen + water system: Compositional analysis of equilibrium phases](#), *Industrial & Engineering Chemistry Research*, 2011, **50**, 4722–4730.

- 167 V. Belandria, A. H. Mohammadi, A. Eslamimanesh, D. Richon, M. F. Sánchez-Mora and L. A. Galicia-Luna, [Phase equilibrium measurements for semi-clathrate hydrates of the \(CO₂+n C₂+tetra-n-butylammonium bromide\) aqueous solution systems: Part 2](#), *Fluid Phase Equilibria*, 2012, **322-323**, 105–112.
- 168 S. P. Kang, H. Lee, C. S. Lee and W. M. Sung, [Hydrate phase equilibria of the guest mixtures containing CO₂, N₂ and tetrahydrofuran](#), *Fluid Phase Equilibria*, 2001, **185**, 101–109.
- 169 S. H. Kim, M. D. Seo, J. W. Kang and C. S. Lee, [Hydrate-containing phase equilibria for mixed guests of carbon dioxide and nitrogen](#), *Fluid Phase Equilibria*, 2011, **306**, 229–233.
- 170 B. Olsen, A. Majumdar and R. Bishnoi, Experimental studies dioxide on hydrate and its systems, *Int. J. of Mat. Eng. for Resources*, 1999, **7**, 17–23.
- 171 W. G. Rho, S. H. Kim, D. W. Cho, J. W. Kang and C. S. Lee, [An experimental and modeling study on incipient hydrate-forming conditions for ternary guests of carbon dioxide, nitrogen and sulfur dioxide](#), *Fluid Phase Equilibria*, 2018, **473**, 127–131.
- 172 S.-C. Sun, C.-L. Liu and Q.-G. Meng, [Hydrate phase equilibrium of binary guest-mixtures containing CO₂ and N₂ in various systems](#), *The Journal of Chemical Thermodynamics*, 2015, **84**, 1–6.
- 173 L. J. Noaker and D. L. Katz, [Gas hydrates of hydrogen sulfide-methane mixtures](#), *Journal of Petroleum Technology*, 1954, **6**, 135–137.
- 174 A. H. Mohammadi and D. Richon, [Hydrate phase equilibria of gaseous mixtures of methane + carbon dioxide + hydrogen sulfide](#), *Chemical Engineering Communications*, 2015, **202**, 629–633.
- 175 Z. T. Ward, R. A. Marriott, A. K. Sum, E. D. Sloan and C. A. Koh, [Equilibrium data of gas hydrates containing methane, propane, and hydrogen sulfide](#), *Journal of Chemical & Engineering Data*, 2015, **60**, 424–428.

- 176 H.-J. Ng and D. B. Robinson, [The role of n-butane in hydrate formation](#), *AIChE Journal*, 1976, **22**, 656–661.
- 177 V. T. John and G. D. Holder, [Hydrates of methane + n-butane below the ice point](#), *Journal of Chemical and Engineering Data*, 1982, **27**, 18–21.
- 178 V. A. Kamath and G. D. Holder, in *Annual AIChE meeting*, Los Angeles, 1982.
- 179 M. A. Behnamotlagh, R. Hashemi, Z. Taheri Rizi, M. Mohammadtaheri and M. Mohammadi, [Experimental study of the effect of the combined monoethylene glycol with NaCl/CaCl₂ salts on sour gas hydrate inhibition with low-concentration hydrogen sulfide](#), *Journal of Chemical & Engineering Data*, 2022, **67**, 1250–1258.
- 180 P. B. Dharmawardhana, W. R. Parrish and E. D. Sloan, [Experimental thermodynamic parameters for the prediction of natural gas hydrate dissociation conditions](#), *Industrial and Engineering Chemistry Fundamentals*, 1980, **19**, 410–414.
- 181 S. Ovalle, C. Martinez and J. G. Beltran, [Phase equilibria of hydrates from ternary mixtures of methane + ethane + propane and methane + propane + carbon dioxide](#), *The Canadian Journal of Chemical Engineering*, 2022, 1–6.
- 182 D. B. Robinson and J. B. Hutton, [Hydrate formation in systems containing methane, hydrogen sulphide and carbon dioxide](#), *Journal of Canadian Petroleum Technology*, 1967, **6**, 6–9.
- 183 J. P. Schroeter, R. Kobayashi and M. A. Hildebrand, [Hydrate decomposition conditions in the system hydrogen sulfide-methane-propane](#), *Industrial & Engineering Chemistry Fundamentals*, 1983, **22**, 361–364.
- 184 C. Y. Sun, G. J. Chen, W. Lin and T. M. Guo, [Hydrate formation conditions of sour natural gases](#), *Journal of Chemical and Engineering Data*, 2003, **48**, 600–602.

- 185 Y. H. Sun, S. L. Li, G. B. Zhang, W. Guo and Y. H. Zhu, [Hydrate phase equilibrium of CH₄+N₂+CO₂ gas mixtures and cage occupancy behaviors](#), *Industrial and Engineering Chemistry Research*, 2017, **56**, 8133–8142.
- 186 Z. G. Sun, S. S. Fan, L. Shi, Y. K. Guo and K. H. Guo, [Equilibrium conditions hydrate dissociation for a ternary mixture of methane, ethane, and propane in aqueous solutions of ethylene glycol and electrolytes](#), *Journal of Chemical and Engineering Data*, 2001, **46**, 927–929.
- 187 X. Zang and D. Liang, [Phase equilibrium data for the hydrates of synthesized ternary CH₄/CO₂/N₂ biogas mixtures](#), *Journal of Chemical and Engineering Data*, 2018, **63**, 197–201.
- 188 M. Cha, K. Shin, J. Kim, D. Chang, Y. Seo, H. Lee and S.-P. Kang, [Thermodynamic and kinetic hydrate inhibition performance of aqueous ethylene glycol solutions for natural gas](#), *Chemical Engineering Science*, 2013, **99**, 184–190.
- 189 R. Kobayashi, H. J. Withrow, G. B. Williams and D. L. Katz, in *Proceedings of the 13th annual convention of natural gasoline association of america*, 1951, pp. 27–31.
- 190 J.-W. Lee and S.-P. Kang, [Phase equilibria of natural gas hydrates in the presence of methanol, ethylene glycol, and NaCl aqueous solutions](#), *Industrial & Engineering Chemistry Research*, 2011, **50**, 8750–8755.
- 191 D. H. Mei, J. Liao, J. T. Yang and T. M. Guo, [Hydrate formation of a synthetic natural gas mixture in aqueous solutions containing electrolyte, methanol, and \(electrolyte + methanol\)](#), *Journal of Chemical and Engineering Data*, 1998, **43**, 178–182.
- 192 I. Wilcox, D. B. Carson and D. L. Katz, Natural hydrates, *Industrial & Engineering Chemistry*, 1941, **33**, 662–665.
- 193 D. B. Robinson and H. J. Ng, [Hydrate formation and inhibition in gas or gas condensate streams.](#), *Journal of Canadian Petroleum Technology*, 1986, **25**, 26–30.

- 194 C. Eichholz, A. Majumdar, M. A. Clarke, L. R. Oellrich and P. R. Bishnoi, [Experimental investigation and calculation of methane hydrate formation conditions in the presence of ethylene glycol and sodium chloride](#), *Journal of Chemical & Engineering Data*, 2004, **49**, 847–851.
- 195 A. H. Mohammadi and D. Richon, [Gas hydrate phase equilibrium in methane + ethylene glycol, diethylene glycol, or triethylene glycol + water system](#), *Journal of Chemical & Engineering Data*, 2011, **56**, 4544–4548.
- 196 H. Haghighi, A. Chapoy, R. Burgess and B. Tohidi, [Experimental and thermodynamic modelling of systems containing water and ethylene glycol: Application to flow assurance and gas processing](#), *Fluid Phase Equilibria*, 2009, **276**, 24–30.
- 197 A. H. Mohammadi and D. Richon, Phase equilibria of methane hydrates in the presence of methanol and / or ethylene glycol aqueous solutions, *Ind. Eng. Chem. Res.*, 2010, **49**, 925–928.
- 198 P. D. Dholabhai, J. Scott Parent and P. Raj Bishnoi, [Equilibrium conditions for hydrate formation from binary mixtures of methane and carbon dioxide in the presence of electrolytes, methanol and ethylene glycol](#), *Fluid Phase Equilibria*, 1997, **141**, 235–246.
- 199 M. A. Aminolroayaei, Z. Taheri Rizi, M. Mohammad-Taheri, A. Kamran Pirzaman, M. Dehbandi Baladehi and M. R. Ehsani, Experimental measurements and thermodynamic modeling of CH₄ + H₂S + MEG hydrate phase-equilibrium conditions at 6.2–12.3 MPa, *Journal of Chemical & Engineering Data*, DOI:[10.1021/acs.jced.2c00111](#).
- 200 H. Haghighi, A. Chapoy, R. Burgess, S. Mazloun and B. Tohidi, [Phase equilibria for petroleum reservoir fluids containing water and aqueous methanol solutions: Experimental measurements and modelling using the CPA equation of state](#), *Fluid Phase Equilibria*, 2009, **278**, 109–116.

201 Q. Nasir, K. K. Lau, B. Lal and K. M. Sabil, [Hydrate dissociation condition measurement of CO₂-rich mixed gas in the presence of methanol/ethylene glycol and mixed methanol/ethylene glycol + electrolyte aqueous solution](#), *Journal of Chemical & Engineering Data*, 2014, **59**, 3920–3926.