Multi-Component-Multiphase Flash Calculations for Systems Containing Gas Hydrates by Direct Minimization of Gibbs Free Energy

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ABSTRACT: *The Michelsen stability and multiphase flash calculation by direct minimization of Gibbs free energy of the system at constant temperature and pressure, was used for systems containing gas hydrates. The solid hydrate phase was treated as a solid solution. The fugacities of all components of the hydrate phase were calculated as a function of compositions by the rearranged model of van der Waals and Platteeuw. Using this rearranged model enables the use of multiphase flash algorithm for systems containing gas hydrates. Based on this calculation for hydrate phases, we can determine amounts of hydrate formed and structure stability based on a minimum Gibbs free energy criterion.*

KEY WORDS: *Flash calculation, Minimization, Gibbs free energy, Equation of state, Gas hydrate.*

INTRODUCTION

Gas hydrates are crystalline solid compounds, which are formed by the combination of light hydrocarbon gases (such as methane, ethane, propane, etc.) or of non hydrocarbon gases (such as carbon dioxide, nitrogen, etc.) with water at temperature near freezing point of water and high pressure. Due to hydrogen bonding of water molecules, some cavities are formed in crystalline network of water molecules. Inclusion of such gases in these cavities and formation of van der Waals forces between gas and water molecules cause the crystalline network of water to be stable. Usually, gas hydrates are formed in three structures sI, sII and sH.

The statistical thermodynamic model for prediction of thermodynamic properties of gas hydrates was first developed by *van der Waals* and *Pelatteeuw* [1]. Prediction of hydrate dissociation condition for gas mixtures has been presented by *Parrish* and *Prausnitz* [2]. *Bishnoi et al.* [3] offered a model for flash calculations for systems containing gas hydrates. *Cole et al.* [4] rearranged the *van der Waals* and *Pelatteeuw* model in order to obtain the fugacities of all components of hydrate phase, including water, to be calculated as a function of

hydrate phase compositions. Cole's method was also used for flash calculations in systems containing gas hydrates.

There are several calculations that could provide important information regarding gas hydrate phases, in addition to the normal pressure-temperature dissociation locus. These include the ability to calculate the amount of hydrate that will form under given circumstances and the ability to calculate the composition of all equilibrium phases. In addition, a method of determining which hydrate structure will form under given conditions according to the thermodynamic stability criterion is also needed.

This work aimed at the calculation of phase fraction and composition of components in equilibrium phases. This was done by direct minimization of Gibbs free energy of the system as a function of composition or mole number of phases at constant temperature and pressure.

TANGENT-PLANE-DISTANCE APPROACH (TPD)

Suppose $\underline{z}$ is a given overall composition. The mathematical expression of the TPD function is:

$$TPD(\underline{x}) = \sum_{i=1}^{NC} x_i \left[\mu_i(\underline{x}) - \mu_i(\underline{z}) \right] \qquad (1\text{-}a)$$

where $TPD(\underline{x})$ is the distance function between the Gibbs free energy surface and its tangent plane at composition $\underline{z}$. When $TPD(\underline{x})$ is minimized with respect to x_i (I=1,2,…,NC) subject to:

$$\sum_{i=1}^{NC} x_i = 1 \qquad (1\text{-}b)$$

$$0 \le x_i \le 1 \qquad (i = 1,2,..., NC) \qquad (1\text{-}c)$$

The optimized value, TPD^*, provides the stability analysis of the mixture at composition $\underline{z}$. If $TPD^* \ge 0$, the system is absolutely stable; if $TPD^* < 0$, the system is unstable.

Differentiation of Eq. (1-a) with respect to NC-1 independent mole fraction yields the stationarity condition (maximum or minimum point):

$$\mu_i(\underline{x}) - \mu_i(\underline{z}) = K \qquad i = 1,2,…, NC \qquad (2)$$

For equation of state calculations it is more convenient to work in terms of fugacity coefficients.

Therefore Eq. (2) can be written as:

$$\ln(x_i) + \ln\left[\phi_i(\underline{x})\right] - \ln(z_i) - \ln\left[\phi_i(\underline{z})\right] = \frac{K}{R\,T} = k \qquad (3)$$

$$i = 1,2,…, NC$$

Introducing new variables $X_i = x_i \exp(-K)$, the new independent variables X_i can formally be interpreted as mole numbers of component i, *Michelsen* [7] showed that Eq. (1-a) can be written as:

$$TPD(\underline{X}) = 1 + \sum_{i=1}^{nc} X_i \begin{pmatrix} \ln(X_i) + \ln\left[\phi_i(\underline{x})\right] \\ -\ln(z_i) - \ln\left[\phi_i(\underline{z})\right] - 1 \end{pmatrix} \qquad (4)$$

where $x_i = \dfrac{X_i}{\displaystyle\sum_{i=1}^{NC} X_i}$

In Eq. (4) X_i is the mole number of component i, and its only constraint is $X_i \ge 0$. Therefore, instead of Eq. (1-a) equation (4) with $X_i \ge 0$ constraint could be minimized, and obtain the TPD^*. $TPD^* < 0$ is equal to $\sum_{i=1}^{NC} X_i > 1$ and system is unstable. If $\sum_{i=1}^{NC} X_i \le 1$, $TPD^* \ge 0$ and system is stable.

The optimized composition $\underline{x}^*$, is a good approximation of the incipient phase composition. When the system is unstable, a good initial composition $\underline{x}^*$ strengthens the convergence of the Newton's method or the successive substitution method.

It should be noted that all components do not enter the hydrate phase. Therefore the equation of the Tangent-Plane Distance for hydrate phase from liquid aqueous phase must be written as:

$$TPD(x) = \sum_{i=1}^{NHF+1} x_i \left[\mu_i(\underline{x}) - \mu_i(\underline{z}) \right] \qquad (5)$$

where NHF+1 is the number of components plus water that can form hydrate. Also the mole fraction of components in hydrate phase can not have any value. According to hydrate structure and component, the value of mole fraction of component in sI hydrate will be between zero and 0.1739, and for sII hydrate will be between zero and 0.17647.

In this work, the Simulated Annealing (SA) algorithm [5,6] was used to minimize the TPD function to test the stability of a mixture.

THREE-PHASE FLASH CALCULATION
Successive substitution method

Consider a system with one mole of feed and overall mole fraction $\underline{z}$. If L, S and V be the amount of liquid, solid and vapor phases with mole fraction $\underline{x}$, $\underline{u}$ and $\underline{y}$, respectively, the mass balance equations are:

$$1 = V + L + S \tag{6}$$

$$z_i = y_i V + x_i L + u_i S \tag{7}$$

elimination of V from Eq. (6) and combining it with Eq. (7) leads to:

$$z_i = y_i(1 - L - S) + x_i L + u_i S \tag{8}$$

if we define the equilibrium ratios as follows:

$$K_{1,i} = \frac{y_i}{x_i} \tag{9}$$

$$K_{2,i} = \frac{u_i}{x_i} \tag{10}$$

combining these two equations with Eq. (8) leads to:

$$x_i = \frac{z_i}{K_{1,i} + L(1 - K_{1,i}) + S(K_{2,i} - K_{1,i})} \tag{11}$$

$$y_i = \frac{K_{1,i}\, z_i}{K_{1,i} + L(1 - K_{1,i}) + S(K_{2,i} - K_{1,i})} \tag{12}$$

$$u_i = \frac{K_{2,i}\, z_i}{K_{1,i} + L(1 - K_{1,i}) + S(K_{2,i} - K_{1,i})} \tag{13}$$

Since the sum of all mole fractions of each phase must be equal to one, hence:

$$\sum_{i=1}^{NC} y_i = \sum_{i=1}^{NC} x_i = \sum_{i=1}^{NC} u_i = 1 \tag{14}$$

then we obtain the following equations:

$$\sum_{i=1}^{NC} (y_i - x_i) = \tag{15}$$

$$\sum_{i=1}^{NC} \frac{z_i(K_{1,i} - 1)}{K_{1,i} + L(1 - K_{1,i}) + S(K_{2,i} - K_{1,i})} = 0$$

$$\sum_{i=1}^{NC} u_i - 1 = \tag{16}$$

$$\sum_{i=1}^{NC} \frac{K_{2,i}\, z_i}{K_{1,i} + L(1 - K_{1,i}) + S(K_{2,i} - K_{1,i})} - 1 = 0$$

Eqs. (15) and (16) can be solved by successive substitution and hence to obtain two variables L and S.

Newton's method

According to Newton's method for three-phase flash calculations, there are 3NC+3 equations and 3NC+3 variables. The equations are as follows:

$$f_i^v = f_i^l \Rightarrow \varphi_i^v y_i P = \varphi_i^l x_i P \Rightarrow \tag{17}$$

$$y_i - \frac{\varphi_i^l}{\varphi_i^v} x_i = 0 \quad, \quad i = 1,..., NC$$

$$f_i^s = f_i^l \Rightarrow \varphi_i^s u_i P = \varphi_i^l x_i P \Rightarrow \tag{18}$$

$$u_i - \frac{\varphi_i^l}{\varphi_i^s} x_i = 0 \quad, \quad i = 1,..., NC$$

$$z_i - y_i V - x_i L - u_i S = 0 \quad, \quad i = 1,..., NC \tag{19}$$

$$\sum_{i=1}^{NC} y_i = 1 \tag{20}$$

$$\sum_{i=1}^{NC} x_i = 1 \tag{21}$$

$$\sum_{i=1}^{NC} u_i = 1 \tag{22}$$

where $\underline{y}$, $\underline{x}$, $\underline{u}$, V, L and S are unknown variables.

Multi-component-multiphase flash calculations by direct minimization of Gibbs free energy

Consider the multicomponent-multiphase flash at constant temperature and pressure. The equilibrium state consist of NP phases; each phase j consist of n_{1j}, n_{2j}, ..., n_{NCj} moles. From the second law of thermodynamics, the equilibrium state is a state in which the Gibbs free energy of the system is a minimum. The minimum of Gibbs free energy is a sufficient and necessary condition for the equilibrium state.

At constant temperature and pressure, the Gibbs free energy of the system can be written as:

$$G = \sum_{j=1}^{NP} G_j \left(n_{1j}, n_{2j}, n_{3j}, \ldots, n_{NCj}\right) \tag{23}$$

where C_j is the Gibbs free energy of phase j, and G is the total Gibbs free energy of the system. When G is minimized with respect to n_{ij}(I= 1,2,..., NC; j=1,2,...,NP) subject to the following constraints:

Material balance of component i

$$H_i = n_i - \sum_{j=1}^{NP} n_{ij} = 0 \quad \left(i = 1,2,\ldots, NC\right) \tag{24}$$

The non-negative mole number of component i in phase j

$$0 \le n_{ij} \le n_i \qquad \left(i = 1,2,\ldots, NC\ ;\ j = 1,2,\ldots, NP\right) \tag{25}$$

the optimized value $n_{ij}^* \left(i = 1,2,\ldots, NC\ ;\ j = 1,2,\ldots, NP\right)$ are the mole numbers of the equilibrium state.

The Gibbs free energy of the system is given by:

$$G = \sum_{j=1}^{NP} \sum_{i=1}^{NC} n_{ij}\, \mu_{ij} \tag{26}$$

where μ_i is given by:

$$\mu_i = \mu_i^0\left(T\right) + R\,T \ln\left(\frac{f_i}{f_i^0\left(T\right)}\right) \tag{27}$$

where $\mu_i^0\left(T\right)$ and $f_i^0\left(T\right)$ are the chemical potential and fugacity in the standard state, respectively. Combining Eqs. (26) and (27) leads to:

$$G = \sum_{i=1}^{NC} n_i \left[\mu_i^0\left(T\right) - R\,T \ln\left(f_i^0\right)\right] + \tag{28}$$

$$R\,T \sum_{i=1}^{NC} \sum_{j=1}^{NP} n_{ij} \ln\left(f_{ij}\right)$$

the first term on the right-hand side of Eq. (28) is a constant and the second term is a function of $n_{ij}\left(i = 1,2,\ldots, NC\ ;\ j = 1,2,\ldots, NP\right)$; therefore, there are NC×NP variables.

The minimization of Gibbs free energy is a constrained minimization problem. The constraints are

Eqs. (24) and (25). Two methods can be used to solve this optimization problem. First, a penalty function method might be used to solve this constrained optimization problem. The basic idea is to convert the constrained problem into a sequence of unconstrained problem [14]. The new objective function is thus:

$$\phi\left(n_{ij}, r\right) = G\left(n_{ij}\right) + \frac{1}{\sqrt{r}} \sum_{i=1}^{NC} \left(H_i\right)^2 = \tag{29}$$

$$\sum_{i=1}^{NC} n_i \left[\mu_i^0\left(T\right) - R\,T \ln\left(f_i^0\right)\right] +$$

$$R\,T \sum_{i=1}^{NC} \sum_{j=1}^{NP} n_{ij} \ln\left(f_{ij}\right) + \frac{1}{\sqrt{r}} \sum_{i=1}^{NC} \left(H_i\right)^2$$

where r is a positive real number, which forms a monotonically decreasing sequence during the process of minimization. Under certain conditions, it can be proven:

$$\lim_{r \to 0} \underline{n}\left(r\right) = \underline{n}^* \tag{30}$$

where $\underline{n}$ is the minimum of the new function ϕ for a given r, and $\underline{n}^*$ is the solution of initial minimization problem (Eq. (23) or (28)). In the second method, we can eliminate the mole numbers of one phase (say, phase 1) from material balance constrains, Eq. (24):

$$n_{i1} = n_i - \sum_{j=2}^{NP} n_{ij} \quad,\quad i = 1,\ldots, NC \tag{31}$$

The minimization of G with the constraints:

$$0 \le n_{ij} \le n_i \quad \left(i = 1,2,\ldots, NC\ ;\ j = 2,3,\ldots, NP\right) \tag{32}$$

Provides $n_{ij}^* \left(i = 1,2,\ldots, NC\ ;\ j = 1,2,\ldots, NP\right)$. The mini-mization is performed with the SA algorithm.

THERMODYNAMIC MODEL
Liquid and gas phase

The PR equation of state was used for calculation of liquid and gas phase fugacity coefficient. The PR EOS [10] is given by:

$$P = \frac{R\,T}{\upsilon - b} - \frac{a}{\upsilon^2 + 2\,b\,\upsilon - b^2} \tag{33}$$

van der Waals one fluid mixing rule is used here for parameters a and b, as follows:

$$a_{mix} = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i \, x_j \, \sqrt{a_i \, a_j} \left(1 - k_{ij}\right) \tag{34}$$

$$b_{mix} = \sum_{i=1}^{NC} x_i \, b_i \tag{35}$$

In this work binary interaction parameter between water and gases was obtained by using experimental Henry's constant of gases in water and following relation. As known from thermodynamics:

$$H_{i,w} = \lim_{x_i \to 0} \frac{f_i}{x_i} = \lim_{x_i \to 0} \frac{\phi_i \, x_i \, P}{x_i} = \tag{36}$$

$$\lim_{x_i \to 0} \left(\phi_i \, P\right) = \lim_{x_i \to 0} \left(\phi_i\right) \lim_{x_i \to 0} \left(P\right) = \phi_i^{\infty} \, P_w^{sat}$$

or

$$\ln\left(H_{i,w}\right) = \ln\left(\phi_i^{\infty}\right) + \ln\left(P_w^{sat}\right) \tag{37}$$

where P_w^{sat} is the vapor pressure of water at specified temperature. The fugacity coefficient of component i in mixture according to PR EOS is given as:

$$\ln \phi_i = \tag{38}$$

$$\frac{b_i}{b_{mix}} \left(\frac{P \, \upsilon_{mix}}{R \, T} - 1 \right) - \ln \left(\frac{P \left(\upsilon_{mix} - b_{mix} \right)}{R \, T} \right) -$$

$$\frac{a_{mix}}{2\sqrt{2} \, b_{mix} \, R \, T} \left[\frac{2 \displaystyle\sum_{j=1}^{NC} x_j \, a_{ij}}{a_{mix}} - \frac{b_i}{b_{mix}} \right]$$

$$\ln \left(\frac{\upsilon_{mix} + 2.414 \, b_{mix}}{\upsilon_{mix} - 0.414 \, b_{mix}} \right)$$

and hence $\ln\left(\phi_i^{\infty}\right)$ will be:

$$\ln \phi_i^{\infty} = \frac{b_i}{b_w} \left(\frac{P_w^* \, \upsilon_w}{R \, T} - 1 \right) - \ln \left(\frac{P_w^* \left(\upsilon_w - b_w \right)}{R \, T} \right) - \tag{39}$$

$$\frac{a_w}{2\sqrt{2} \, b_w \, R \, T} \left[\frac{2 \, a_{iw}}{a_w} - \frac{b_i}{b_w} \right] \ln \left(\frac{\upsilon_w + 2.414 \, b_w}{\upsilon_w - 0.414 \, b_w} \right)$$

where subscript w stands for water. Binary interaction parameter between water and gas k_{iw}, can be found by

fitting experimental Henry's constant data of gases in water with Eq. (37).

Hydrate phase

The simplified method of *Cole et al.* [4] by *Michelsen* [11] was used for calculation of fugacity of components of hydrate phase. Detailed description of this method has been mentioned in those references.

Hypothetical empty hydrate lattice phase

For calculation of fugacity of water in hydrate phase it is necessary to calculate fugacity of water in hypothetical empty hydrate phase. The fugacity of water in the empty hydrate lattice was calculated as a function of temperature and pressure following the method outlined by *Anderson et al.* [12]. If temperature is below the ice point, we define:

$$\Delta\mu_w^{\beta-\alpha} = \Delta\mu_w^{\beta} - \Delta\mu_w^{\alpha} \tag{40}$$

and if temperature is above the ice point, we define:

$$\Delta\mu_w^{\beta-L} = \mu_w^{\beta} - \mu_w^{L} \tag{41}$$

we calculated f_w^{β} from:

$$f_w^{\beta} = f_w^{\alpha} \exp\left(\frac{\Delta\mu_w^{\beta-\alpha}}{R \, T} \right) \tag{42}$$

or

$$f_w^{\beta} = f_w^{L} \exp\left(\frac{\Delta\mu_w^{\beta-L}}{R \, T} \right) \tag{43}$$

where f_w^{α} and f_w^{L} are the fugacities of water as ice or pure liquid water. The chemical potential difference defined by Eqs. (40) and (41) was calculated using the method outlined by *Holder et al.* [16]:

$$\frac{\Delta\mu_w^{\beta-\alpha}}{R \, T} = \frac{\Delta\mu_w^{0}}{R \, T^0} - \int_{T^0}^{T} \frac{\Delta h_w^{\beta-\alpha}}{R \, T^2} dT + \int_{0}^{P} \frac{\Delta\upsilon_w^{\beta-\alpha}}{R \, T} dP \tag{44}$$

or

$$\frac{\Delta\mu_w^{\beta-L}}{R \, T} = \frac{\Delta\mu_w^{0}}{R \, T^0} - \int_{T^0}^{T} \frac{\Delta h_w^{\beta-L}}{R \, T^2} dT + \tag{45}$$

$$\int_{0}^{P} \frac{\Delta\upsilon_w^{\beta-L}}{R \, T} dP + \ln\left(\gamma_w \, x_w\right)$$

Table 1: Equilibrium mole and phase fraction for ternary system methane-propane-water a 274 K.

	P (MPa)	T (K)	Compositions V	Compositions La	Compositions HII	Phase Fraction V	Phase Fraction La	Phase Fraction HII	Compositions[a] V	Compositions[a] La	Compositions[a] HII	Phase Fraction[a] V	Phase Fraction[a] La	Phase Fraction[a] HII
Methane			0.99765	0.0000209	0.0000				-	-	-			
Propane	2.1	274	0.00200	0.0000001	0.0000	0.5002	0.4998	0	-	-	-	-	-	-
Water			0.00035	0.999979	0.0000				-	-	-			
Methane			0.99851	0.00002	0.11677				0.9981	0.0008	0.1140			
Propane	2.5	274	0.00118	0.00000	0.01651	0.4965	0.4759	0.0277	0.0016	0.00	0.0191	-	-	-
Water			0.00031	0.99998	0.86672				0.0003	0.9992	0.8669			
Methane			0.9996	0.00003	0.13241				-	-	-			
Propane	2.9	274	0.00011	0.00000	0.00218	0.4432	0.1339	0.4229	-	-	-	-	-	-
Water			0.00029	0.99997	0.86541				-	-	-			

a) these values were reported in ref. [3].

Table 2: Equilibrium phase and mole fractions for sII hydrate in equilibrium with gas phase
at pressure 1000 kPa for ternary system methane-propane-water.

|	P (KPa)	T (K)	Composition V	Composition HsII	Phase Fraction V	Phase Fraction HsII	Composition[a] V	Composition[a] HsII	Phase Fraction[a] V	Phase Fraction[a] HsII
Methane			0.95462	0.07448			0.9544	0.0766		
Propane	1000	268	0.04503	0.04954	0.8966	0.1034	0.0452	0.048		0.1034
Water			0.00035	0.87598			0.00044	0.8755		
Methane			0.95454	0.07292			0.9545	0.0727		
Propane	1000	270	0.04504	0.04950	0.8968	0.1032	0.045	0.0494		0.1030
Water			0.00042	0.87758			0.0005	0.8779		
Methane			0.9544	0.07052			-	-		
Propane	1000	273	0.04505	0.04944	0.8976	0.1024	-	-	-	-
Water			0.00055	0.88004			-	-		
Methane			0.95429	0.06890			-	-		
Propane	1000	275	0.04506	0.04938	0.8976	0.1024	-	-	-	-
Water			0.00065	0.88172			-	-		

a) these values were reported in ref. [4].
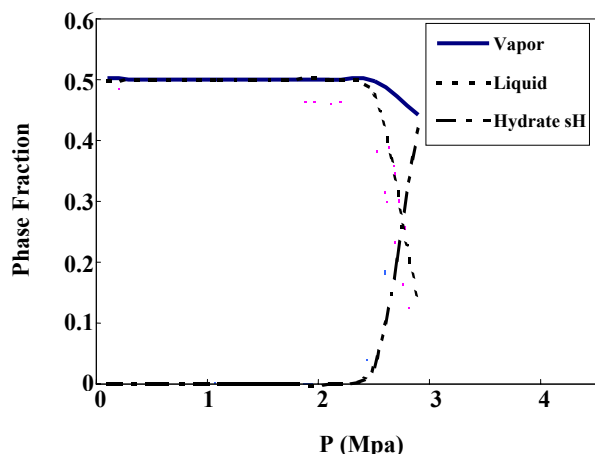
Fig. 1: Equilibrium phase fraction at temperature 274 K and various pressure for ternary system, methane-propane-water.

CALCULATIONS AND RESULTS

This method was used for the ternary system, methane, propane and water. The mole fractions of methane, propane and water were 0.499, 0.001 and 0.50, respectively. Binary interaction parameters between methane-propane, methane-water and propane-water were 0.00748, -0.08728 and -0.15913, respectively. For this system, equilibrium phase fraction has been shown in Fig. 1. Also table 1 shows equilibrium mole and phase fraction at temperature 274 K and pressures 2.1, 2.5 and 2.9 MPa.

Table 2 shows some results of flash calculation for ternary system, methane-propane-water which their compositions were 0.8636, 0.0455 and 0.0909, respectively. These calculations were done at various temperatures and 1000 KPa pressure and the equilibrium phase and mole fractions are listed in table 2. All calculations were done for *sII* hydrate.

CONCLUSIONS

In this work the phase stability analysis was used for systems containing gas hydrate and multiphase equilibrium computations can be performed very reliably, by direct minimization of Gibbs free energy by use of the powerful algorithm of simulated annealing. Initial guesses obtained by stability analysis, were used for two and three phase flash calculations for systems containing gas hydrate. These calculations showed that the hydrate structure and equilibrium phase compositions can be predicted by this method. This calculation can provide an

in depth understanding of the phase behavior of such complex systems.

Nomenclature

a	Equation of state parameter
b	Equation of state parameter
f	Fugacity
G	Total Gibbs free energy
h	Molar enthalpy
H	Henry's constant
k_{ij}	Binary interaction parameter
k	Dimensionless chemical potential difference
K	Chemical potential difference
K	Equilibrium ratio
L	Liquid phase fraction
n	Mole number
NC	Number of components
NHF	Number of components that can form hydrate
NP	Number of phases
P	Pressure
r	Penalty factor
R	Universal gas constant
S	Solid phase fraction
T	Absolute temperature
TPD	Tangent plane distance function
$\underline{u}$	Vector of composition of solid phase
V	Vapor phase fraction
$\underline{x}$	Vector of composition of liquid phase
X	Mole number vector
$\underline{y}$	Vector of composition of gas phase
$\underline{z}$	Overall vector of composition

Greek Letters

μ	Chemical potential
φ	Fugacity coefficient
υ	Molar volume

Superscripts and Subscripts

0	Standard state
αβ	Ice phase
β	Hypothetical empty hydrate lattice phase
β-α	Difference between empty hydrate lattice and ice
β-L	Difference between empty hydrate lattice and pure liquid water

v	Vapor phase
l	Liquid phase
L	Pure liquid water phase
s	Solid phase
sat	Saturation condition
*	Optimized value
∞	Infinite dilution
i,j	Component
j	Phase
mix	Mixture
w	Water

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