

# Phase Equilibria in the Formation of Hydrates in Methane or Carbon Dioxide + Water Systems Using Isofugacity and Gibbs Energy Minimization

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Gas hydrates are crystalline structures formed by water molecules and compounds of low molecular weights, being formed under suitable conditions of pressure and temperature. Although initially considered as inconveniences to the natural gas industries, they are currently considered as promising alternatives for solving some important global issues, such as contributing to the reduction of effects caused by the greenhouse gases. This concern related to the control of emissions of polluting gases has mobilized hundreds of countries that, at the United Nations Climate Change Conference (COP), agreed to reduce emissions of carbon dioxide and other gases by 2100. However, despite several strategies in the reduction of carbon dioxide emissions have been proposed, many rely on political incentives and substantial investments to convert pre-existing technologies to clean technologies, making such applicability and adaptability problematic. Thus, innovative Carbon Capture and Storage (CCS) techniques are being studied, which considers the use of gas hydrates formation to trap these gases, presents perspectives of lower costs and low environmental damages, promising to overcome the above mentioned problem, besides capturing and storing adequately the carbon dioxide and methane emitted. The need for robust evaluation of the thermodynamic equilibrium of hydrate-containing systems arises in order to make the proposal feasible and used on a large scale. The present work extensively solidifies this assessment of hydrate phase equilibria by proposing the isofugacity and Gibbs energy minimization criteria coupled to the nonlinear programming for the calculation of phase equilibria in the formation of methane and carbon dioxide hydrates. The Soave-Redlich-Kong cubic equation (SRK) was used to calculate the liquid and gaseous phases, and the Van der Waals and Platteeuw models were used to describe the solid phase of the hydrate. The procedure was implemented in the General Algebraic Modeling System (GAMS) software and in the CONOPT3 solver, with some numerical procedures performed in Microsoft Office Excel. The comparison between the results obtained from the present study by the isofugacity criterion and experimental data has been carried out, allowing concluding the satisfactory prediction of the phase equilibria behavior of systems containing hydrates.

## 1. Introduction

Hydrates are non-stoichiometric crystalline structures formed by water molecules and compounds of low molecular weights, being formed under high pressures and low temperatures conditions. The hydrogen bonds between aqueous molecules form solid cavities that encage one or more guests compounds. These compounds, in its turn, stabilize the crystal structure by interacting with water molecules from Van der Waals-type interactions (Sloan and Koh, 2008).

Due to the large gas storage capacity, in which 1 m<sup>3</sup> of hydrate can contain approximately 180 m<sup>3</sup> of gas (Gudmundsson et al., 1994), it is feasible for these crystals, based on the CCS – Carbon Capture and Storage – methodology, to adequately encage and dispose waste gases from matter transformation processes, substantially problematic to the greenhouse effect, such as methane and carbon dioxide.

Therefore, this methodology can provide a safe, economical, practical and potentially promising alternative for solving this important global issue (Rackley, 2017), which urgency have been mobilizing hundreds of countries in recent years (Balibar, 2017).

Although feasible in theory, this and other processes involving hydrates require further studies to consolidate the methodological knowledge as a whole, making the technologies highly efficient and attractive on a large scale. Thus, a solidified and fully evaluation of the thermodynamic equilibrium prediction of hydrate systems is required.

The criteria of equilibrium in closed systems corresponds to a well-established condition in thermodynamic and can be solved in several equivalent ways, in which isofugacity is the most commonly used methodology for calculation. However, a second methodological procedure concerning the Gibbs energy minimization has also been used, which allows the prediction of phase equilibria under more general situations, for example when not all phases are formed.

This second procedure makes no distinction between the phases in the system and becomes feasible by focusing the calculations on the chemical potential value of the constituent species (White et al., 1958) under constant temperature and pressure conditions. The existence of the phases and the composition of each phase are determined only after the method completion.

This methodology, coupled with a suitable algorithm and the use of robust software for subsequently resolution, could assure that a global optimum is achieved if both the sufficient and necessary conditions for the minimization of the Gibbs energy are met. Since in this paper a convexity analysis was not done, the software GAMS/CONOPT only guarantees a local optimum in the study of hydrate formation, which however is adequate for this work.

## 2. Methodology

### 2.1 Isofugacity

The liquid and vapor phases of the systems in this study were described by the SRK cubic equation of state, represented in the explicit form by Eq(1).

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (1)$$

The fugacity coefficient of the  $i$ -component in the liquid and vapor phases in the mixture were subsequently determined by Eq(2), represented in its generalized form (Prausnitz et al., 1999).

$$\ln \hat{\phi}_i = \frac{1}{RT} \left[ \int_V^\infty \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_{j \neq i}} - \frac{RT}{V} \right] dV - \ln Z \quad i = 1, 2, \dots, NC \quad (2)$$

Using the phi-phi approach to determine the fugacity of the  $i$ -component in the liquid and vapor phases in the mixture, then Eq(3) can be applied, for each corresponding phase.

$$\hat{f}_i = x_i \hat{\phi}_i P \quad (3)$$

The proposed methodology for the solid phase modeling was based on the equations developed by Waals and Platteeuw (1959). Thus, the fugacity of water in the hydrate crystalline structure can be calculated by Eq(4).

$$\hat{f}_w^H = f_w^0 \cdot \exp \left[ \sum_{m=1}^{NCAV} \vartheta_m \cdot \ln \left( 1 - \sum_{i=1}^{NC-1} \theta_i^{H,m} \right) + \frac{\Delta \mu_0}{RT_0} + \frac{\Delta H_0}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) - \frac{\Delta C_p}{R} \left[ \ln \left( \frac{T}{T_0} \right) + \frac{T_0}{T} - 1 \right] + \frac{P \Delta V_0}{R \bar{T}} \right] \quad (4)$$

In this equation, all the NCAV different types of cavities that can be formed by nonaqueous components in the system are added. The  $\Delta \mu_0$ ,  $\Delta V_0$ ,  $\Delta H_0$  and  $\Delta C_p$  terms are determined by crystallographic studies and the respective values of these properties used in this work, calculated from a pure water state as ice or liquid to a I or II possible structure that can be formed corresponding to a metastable intermediate crystalline phase, were obtained by Pedersen et al. (2014) and Parrish and Prausnitz (1972). The  $\bar{T}$  term accounts the temperature dependence in the PV/T term, being calculated as the average between the system temperature and the  $T_0$  reference temperature equivalent to 273.15 K. Thus,  $\vartheta_m$  corresponds to the number of cavities of type  $m$  by water molecule, also obtained by the reported values from Pedersen et al. (2014), and  $\theta_i^{H,m}$  denotes the fractional occupancy of molecule  $i$  in cavity  $m$ , being calculated as Eq(5).

$$\theta_{i_m} = \frac{C_{i_m} \hat{f}_i}{1 + \sum_{j=1}^{NC} C_{j_m} \hat{f}_j} \quad i = 1, \dots, NC - 1 \quad (5)$$

The determination of  $C_{i_m}$  for the  $i$ -component in a cavity of type  $m$  is represented by Eq(6) based on the Langmuir model of gas adsorption, in which the simplification was proposed by Munck et al. (1988).

$$C_{i_m} = \frac{A_{i_m}}{T} \cdot \exp\left(\frac{B_{i_m}}{T}\right) \quad (6)$$

The A and B parameters values were obtained by Pedersen et al. (2014) and Parrish and Prausnitz (1972). The iterative numerical procedure used to equal the fugacities between the same components in the different conditions (solid, liquid and vapor) in order to consolidate the isofugacity criterion had been carried out with the aid of Microsoft Office Excel 2010.

## 2.2 Gibbs Energy Minimization

The integration of the partial molar Gibbs energy equation over all gas or vapor phase (V), liquid phase (L) and stable crystalline phase for solid hydrate (H) and also over all the NC components of the system, considering isobaric and isothermal conditions, results in Eq(7).

$$G = \sum_{i=1}^{NC} (n_i^V \mu_i^V + n_i^L \mu_i^L) + \sum_{i=1}^{NC-1} \sum_{m=1}^{NCAV} (n_i^{H,m} \mu_i^{H,m}) + (n_w^H \mu_w^H) \quad (7)$$

For all the liquid and vapor phases, the chemical potential for the  $i$ -component in the mixture can be calculated from a convenient reference state (ideal gas at 1 atm and  $T$ ) to the chemical potential under the system conditions  $T$  and  $P$ , represented by Eq(8).

$$\mu_i(T, P) - \mu_i^0(T, P_0) = RT \cdot \ln\left(\frac{x_i \hat{\phi}_i P}{P_0}\right) \quad (8)$$

where  $P_0$  is 1 atm (1.013 bar). The chemical potential calculation for the guests molecules in the crystalline structure of the hydrate is calculated by Eq(9) for each  $i$ -component encaged in each cavity of type  $m$  in the crystalline structure.

$$\mu_i^{H,m} = \mu_i^0 + \Delta G_i^{m^0} + RT \cdot \ln\left(\frac{\theta_i^{H,m}}{1 - \sum_{i=1}^{NC-1} \theta_i^{H,m}}\right) \quad (9)$$

The value of  $\Delta G_i^{m^0}$  are given by Eq(10).

$$\Delta G_i^{m^0} = -RT \cdot \left[ \ln\left(\frac{A_{i_m}}{T}\right) + \frac{B_{i_m}}{T} \right] \quad (10)$$

The fractional occupancy of molecule  $i$  in cavity  $m$  for any situation is defined by Eq(11), in which  $n_i^{H,m}$  denotes the moles number of the  $i$ -component in the crystalline structure of the hydrate.

$$\theta_i^{H,m} = \frac{n_i^{H,m}}{\vartheta_m \cdot n_w^H} \quad i = 1, \dots, NC - 1 \quad (11)$$

The chemical potential calculation for water in the crystalline structure of the hydrate is based, in its turn, in the Waals and Platteeuw (1959) equation, represented by Eq(12).

$$\mu_w^H = \mu_w^\beta + RT \cdot \sum_{m=1}^{NCAV} \vartheta_m \cdot \ln\left(1 - \sum_i \theta_i^{H,m}\right) \quad (12)$$

The chemical potential values for the components in the standard state ( $\mu_i^0$ ), at  $T$  and  $P_0$ , are calculated from values reported by Atkins and Paula (2006) in a pure state at 298.15 K and 1.013 bar. On the other hand, the chemical potential value for water in the metastable intermediate crystalline phase ( $\mu_w^\beta$ ) was determinate by Eq(13).

$$\mu_w^\beta = \mu_w^L + \Delta \mu_0 \left(\frac{T}{T_0}\right) + \Delta H_0 \left(1 - \frac{T}{T_0}\right) - T \Delta c_p \left[ \ln\left(\frac{T}{T_0}\right) + \frac{T_0}{T} - 1 \right] + \frac{PT \Delta V_0}{RT} \quad (13)$$

where  $T_0$  is 273.15 K,  $\mu_w^L$  is the chemical potential of pure liquid water at  $T$ , and  $\bar{T}$  is the average between  $T$  and  $T_0$ . The substitution of Eq(8), Eq(9) and Eq(12) in Eq(7) results in the nonlinear objective function of the problem, represented by Eq(13).

$$\begin{aligned}
 G(T, P, n_i^k) = & \sum_{i=1}^{NC} n_i^V [\mu_i^0 + RT \cdot \ln(y_i \hat{\phi}_i^V P)] + \sum_{i=1}^{NC} n_i^L [\mu_i^0 + RT \cdot \ln(x_i \hat{\phi}_i^L P)] \\
 & + \sum_{i=1}^{NC-1} \sum_{m=1}^{NCAV} n_i^{H,m} \left[ \mu_i^0 + \Delta G_i^{m0} + RT \cdot \ln \left( \frac{\theta_i^{H,m}}{1 - \sum_{i=1}^{NC-1} \theta_i^{H,m}} \right) \right] \\
 & + n_w^H \left[ \mu_w^\beta + RT \sum_{m=1}^{NCAV} \vartheta_m \cdot \ln \left( 1 - \sum_{i=1}^{NC-1} \theta_i^{H,m} \right) \right]
 \end{aligned} \tag{14}$$

The restrictive conditions of the problem express the molar balance for the  $i$ -nonaqueous components in all the system phases, the molar balance for water also in all the system phases and the non-negativity of number of moles of any component at any phase. This conditions were respectively described by Eq(15), Eq(16) and Eq(17).

$$n_i^V + n_i^L + n_i^{H,s} + n_i^{H,l} = n_i^T \quad i = 1, \dots, NC - 1 \tag{15}$$

$$n_w^V + n_w^L + n_w^H = n_w^T \tag{16}$$

$$n_i^k \geq 0 \tag{17}$$

The resolution of the nonlinear problem was performed using version 23.9.5 of GAMS software, with the CONOPT solver, which uses the Generalized Reduced Gradient optimization technique.

After minimizing the objective function under restrictions (15)-(17) and Eq(11),  $\theta_i^{H,m}$  is equal to the value given by Eq(5), since the necessary condition is the thermodynamic equilibrium. This can be proven mathematically, that the Langmuir isotherm given by Eq(5) is automatically satisfied when the necessary conditions are met.

### 3. Results and Discussion

Figures 1a and 2a represent the phase equilibria respectively determined for the  $\text{CH}_4 + \text{H}_2\text{O}$  and  $\text{CO}_2 + \text{H}_2\text{O}$  systems using both isofugacity and Gibbs energy minimization criteria.

The validation of results were represented by Figures 1b and 2b for the  $\text{CH}_4 + \text{H}_2\text{O}$  and  $\text{CO}_2 + \text{H}_2\text{O}$  systems, respectively. For the first system, the experimental pressures were reported by Dickens and Hunt (1994), Fray et al. (2010), Gayet et al. (2005) and Marshall et al. (1964). For the second system, the experimental pressures were reported by Adisasmito et al. (1991), Fan and Guo (1999), Mohammadi and Richon (2008), Ng and Robinson (1985) and Yasuda and Ohmura (2008).

For both binary systems, the geometric representation of the thermodynamic equilibrium curve as a function of pressure and temperature calculated by isofugacity criterion denotes the existence of simultaneous three phases, among them the hydrate solid phase. The entire length above the curves corresponds to the binary region of hydrate stability; on the other hand, the one below the curves does not show hydrate crystal formation, being in equilibrium only nonaqueous component and water. The deviations from experimental values do not show a regular pattern, but appears to be random, for the different temperature and pressure conditions, not exceeding deviations of 3.00 % in almost all cases. Despite the satisfactory results, the isofugacity methodology is limited to the situations were all phases exist in the system. Thus, the Gibbs energy minimization criterion was presented as a complementary and alternative method to the isofugacity. By randomly considering 3 temperature and pressure conditions away from the previously calculated three-phase equilibrium, thus designating the geometric points 1 to 3 in the graphics, the phase equilibrium was contemplated using the second methodological procedure. Subsequently, for each investigated condition, the results obtained for the molar composition of the components through all the equilibrium phases for  $\text{CH}_4 + \text{H}_2\text{O}$  and  $\text{CO}_2 + \text{H}_2\text{O}$  systems were respectively represented by Tables 1 and 2. The results allow concluding that in point 1, for both systems, the number of moles of the respective nonaqueous component and water in the hydrate structure equals to zero. Therefore, this solid phase that denotes hydrate is not formed, being in equilibrium only  $\text{CH}_4$  or  $\text{CO}_2$  in vapor phase and  $\text{H}_2\text{O}$  in liquid phase. Indeed, this area is located outside the region of hydrate stability, below the range of three phase equilibrium previously calculated by isofugacity criterion. On the other hand, the geometric points of numbers 2 and 3, for both systems, denote existence of the solid phase (hydrate), nonaqueous component in vapor phase and inexistence of water in liquid phase,

reiterating the fact that this region corresponds to the biphasic region of hydrate stability, being located above the range of three phase equilibrium previously calculated by isofugacity criterion. The results also reproduce the non-stoichiometric property of hydrates. In the Gibbs energy minimization, the simulations ensured that all the water was used for the formation of hydrate and the excess nonaqueous component remained in the vapor phase, thus designating one of the two-phase equilibrium regions.

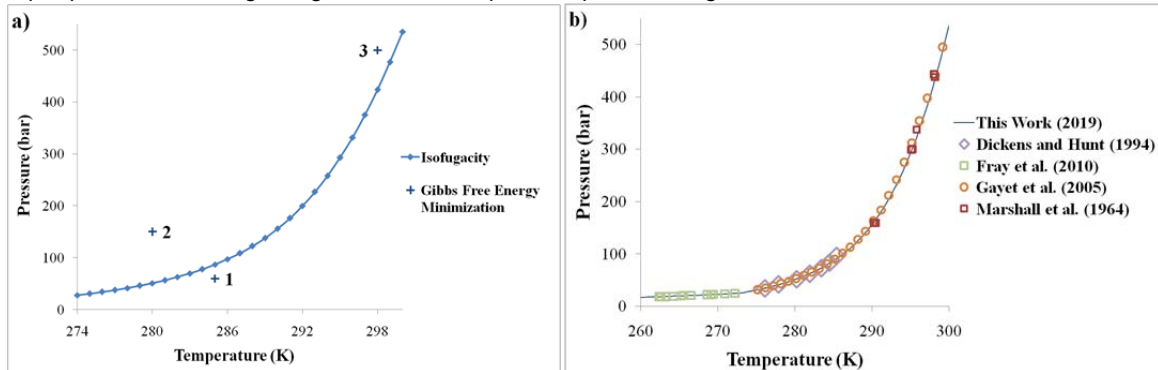


Figure 1. a) Results obtained for the  $\text{CH}_4 + \text{H}_2\text{O}$  system by the isofugacity and Gibbs energy minimization criteria; b) Comparison of calculated values with corresponding experimental values reported in literature.

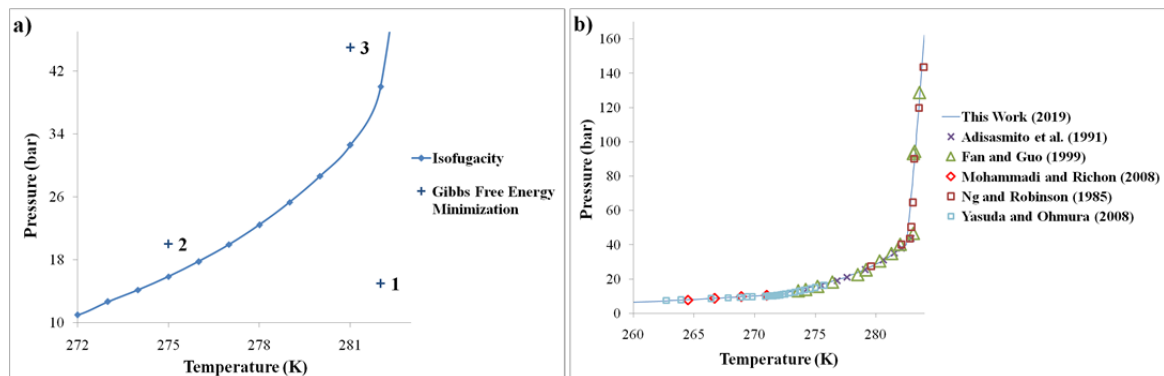


Figure 2. a) Results obtained for the  $\text{CO}_2 + \text{H}_2\text{O}$  system by the isofugacity and Gibbs energy minimization criteria; b) Comparison of calculated values with corresponding experimental values reported in literature.

Table 1: Molar quantities for  $\text{CH}_4$  and  $\text{H}_2\text{O}$  in the geometric points

N.	Comp.	T (K)	P (bar)	Gas	Liquid	sl – small	sl – large	sl-structural
1	$\text{H}_2\text{O}$	285.0	60.0	0	10.000	-	-	-
	$\text{CH}_4$			10.000	0	-	-	-
2	$\text{H}_2\text{O}$	280.0	150.0	0	0	-	-	10.000
	$\text{CH}_4$			8.332	0	0.370	1.297	-
3	$\text{H}_2\text{O}$	298.0	500.0	0	0	-	-	10.000
	$\text{CH}_4$			8.296	0	0.403	1.300	-

Table 2: Molar quantities for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the geometric points

N.	Comp.	T (K)	P (bar)	Gas	Liquid	sl – small	sl – large	sl-structural
1	$\text{H}_2\text{O}$	282.0	15.0	0	10.000	-	-	-
	$\text{CO}_2$			10.000	0	-	-	-
2	$\text{H}_2\text{O}$	275.0	20.0	0	0	-	-	10.000
	$\text{CO}_2$			8.533	0	0.179	1.288	-
3	$\text{H}_2\text{O}$	281.0	45.0	0	0	-	-	10.000
	$\text{CO}_2$			8.524	0	0.182	1.294	-

#### 4. Conclusions

An extensive evaluation of the thermodynamic equilibrium for  $\text{CH}_4 + \text{H}_2\text{O}$  and  $\text{CO}_2 + \text{H}_2\text{O}$  systems was developed in this work, allowing in all of them the possibility of hydrate crystals formation. The stable equilibrium was described based on the isofugacity and Gibbs energy minimization criteria, with a solid description of all equations used. The comparative studies showed that intrinsic limitations related to the equation of state and to the statistical models used did not affect the simulated results, in which deviations lower to 3.000% were obtained in almost all cases in relation to experimental data reported in literature. Thus, it can be stated that the thermodynamic modelling of vapor and liquid phases using the SRK cubic equation of state and the thermodynamic modelling of water in the solid phase (hydrate) based on the Van der Waals and Platteeuw equations was sufficient and very accurate to describe the thermodynamic equilibrium using the isofugacity criterion for all the study systems. It must be emphasized that the formulated algorithms for both methodologies are not limited to the reported results, being able to describe the phase equilibria of the approached systems under different temperature and pressure conditions, making it feasible not only in the academic area, but also in a broad industrial field highly applicable.

#### References

- Adisasmito S., Frank R.J., Sloan E.D., 1991, Hydrates of Carbon Dioxide and Methane Mixtures, *Journal of Chemical & Engineering Data*, 36, 68 – 71.
- Atkins P.W., Paula J. (Eds), 2006, *Physical Chemistry*, W.H. Freeman and Company, New York, NY.
- Balibar S., 2017, Energy Transitions after COP 21 and 22, *Comptes Rendus Physique*, 18, 479 – 487.
- Dickens G.R., Hunt M.S.Q., 1994, Methane Hydrate Stability in Seawater, *Geophysical Research Letters*, 21, 2115 – 2118.
- Fan S.S., Guo T.M., 1999, Hydrate Formation of  $\text{CO}_2$ -Rich Binary and Quaternary Gas Mixtures in Aqueous Sodium Chloride Solutions, *Journal of Chemical & Engineering Data*, 44, 829 – 832.
- Fray N., Marboeuf U., Brissaud O., Schmitt B., 2010, Equilibrium Data of Methane, Carbon Dioxide, and Xenon Clathrate Hydrates below the Freezing Point of Water. Applications to Astrophysical Environments, *Journal of Chemical & Engineering Data*, 55, 5101 – 5108.
- Gayet P., Dicharry C., Marion G., Graciaa A., Lachaise J., Nesterov A., 2005, Experimental Determination of Methane Hydrate Dissociation Curve up to 55MPa by Using a Small Amount of Surfactant as Hydrate Promoter, *Chemical Engineering Science*, 60, 5751 – 5758.
- Gudmundsson J.S., Parlaktuna M., Khokhar, A.A., 1994, Storage of Natural Gas as Frozen Hydrate, *SPE Production & Facilities*, 9, 69 – 73.
- Marshall D.R., Saito S., Kobayashi R., 1964, Hydrates at High Pressures: Part 1. Methane-Water, Argon-Water, and Nitrogen-Water Systems, *AIChE Journal*, 10, 202 – 205.
- Mohammadi A.H., Richon D., 2008, Equilibrium Data of Nitrous Oxide and Carbon Dioxide Clathrate Hydrates, *Journal of Chemical & Engineering Data*, 54, 279 – 281.
- Munck J., Jorgensen S.S., Rasmussen P., 1988, Computations of the Formation of Gas Hydrates, *Chemical Engineering Science*, 43, 2661 – 2672.
- Ng H.J., Robinson D.B., 1985, Hydrate Formation in Systems Containing Methane, Ethane, Propane, Carbon Dioxide or Hydrogen Sulfide in the Presence of Methanol, *Fluid Phase Equilibria*, 21, 145 – 155.
- Parrish W.R., Prausnitz J.M., 1972, Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures, *Industrial & Engineering Chemistry Process Design and Development*, 11, 26 – 35.
- Pedersen K.S., Christensen P.L., Shaikh J.A. (Eds), 2014, *Phase Behavior of Petroleum Reservoir Fluids*, Taylor & Francis Group, Boca Raton, FL.
- Prausnitz J.M., Lichtenthaler R.N., Azevedo E.G. (Eds), 1999, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice Hall PTR, Upper Saddle River, NJ.
- Rackley S.A. (Ed), 2017, *Carbon Capture and Storage*, Butterworth-Heinemann, Oxford, UK.
- Sloan E.D., Koh C.A. (Eds), 2008, *Clathrate Hydrates of Natural Gases*, CRC Press, New York, NY.
- Waals J.H.V., Platteeuw, J.C., 1959, Clathrate Solutions, In: I. Prigogine (Ed), *Advances in Chemical Physics*, Vol 2, Interscience Publishers, New York, NY, 1 – 58.
- White W.B., Johnson S.M., Dantzig G.B., 1958, Chemical Equilibrium in Complex Mixtures, *The Journal of Chemical Physics*, 28, 751 – 755.
- Yasuda K., Ohmura R., 2008, 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*, 53, 2182 – 2188.