



Thermodynamic Modeling of Gas Hydrate Systems for Post-combustion CO₂ Capture with Different Equation of States

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Abstract

In this work, the Claude and Sandler's model was used to predict the equilibrium conditions of gas hydrates in the presence of carbon dioxide and flue gas mixture. Four common equation of states (PR, SRK, PT and VPT) have been used to calculate the thermodynamic properties. The studied temperature range was 273 to 283 K. Results show, although all equation of states can predict the hydrate dissociation conditions of carbon dioxide as well, their prediction ability for flue gas mixture has to be compromised. In addition, it has been concluded VPT equation of state can estimate the hydrate conditions of the flue gas mixture better than other equations.

Keywords: Thermodynamic Modeling, Hydrate, Flue gas, Carbon dioxide, Fugacity, EOS

Introduction

Carbon dioxide, as a major greenhouse gas, plays a pivotal role in climate changes and global warming. The most important source of carbon dioxide emission is the combustion of fossil fuels. CO₂ capture and storage is an effective way of reducing the greenhouse effect.

Post-combustion CO₂ capture refers to the treatment of flue gas before being released into the atmosphere. Flue gas from the power plant usually consists of 15 to 20 mole % CO₂, 5 to 9 mol % O₂, trace gases, and balance N₂ [1]. Among the CO₂ capture and storage technologies, hydrate-based CO₂ capture is a promising method because of the simplicity of the process, small energy penalty, low energy consumption and environmental issues [1-6]. Neglecting impurities, flue gas can be simplified as ternary CO₂, O₂, and N₂ mixture. Furthermore, it can be assumed that the flue gas is the binary mixture of CO₂ and N₂ because of the hydrate formation characteristic of O₂ (such as hydrate formation pressure). As simple hydrates, CO₂ and N₂ form structure I (SI) and structure II (SII), respectively. The structure of CO₂/N₂ mixture hydrate is considered to be either SI or SII depending on the relative ratio of these two different gas molecules occupied in the small and large cavities [1]. For a gas mixture of more than 10% CO₂ and rest N₂, the hydrate structure formed is structure I [7].

To know the mechanism of hydrate formation and to overcome some technical problems, the thermodynamic evaluation of hydrate formation needs to be well understood. In 1959, Vander Waals and Platteuw [8] derived the basic statistical thermodynamic model as the first tool to calculate pure gas hydrate dissociation. Most thermodynamic models are various modifications of the vdW-P model. Parrish and Prausnitz [9] extended the vdWP theory to



study multi-component gas mixtures as guest molecules in the clathrate systems. Klauda and Sandler [10,11] developed a fugacity based approach where the fugacity of water in the hydrate phase has been computed from the chemical potential reported by Parrish and Prausnitz [9]. This approach has been successfully implemented to predict the phase behavior of both single and multiple gas component clathrate hydrates.

In this study, we have employed the Klauda and Sandler model [4] for predicting three phases (L-H-V) equilibria of CO₂ and simulated flue gas hydrates using van der Waals-Platteeuw solid solution theory. The different equations of state (Peng-Robinson (PR) [12], Soave-Redlich-Kwong (SRK) [13] Patel-Teja (PT) [14], Valderrama-Petal-Teja (VPT) [15]) and along with Van der Waals mixing rule [16] are applied in calculating fugacities in vapor phases. Finally, we compare the results of our model with experimental data from the literature [17-30]

Thermodynamic Modeling

We have modeled the three-phase (L-H-V and I-H-V) equilibria of gas hydrates using the fugacity based approach of Klauda and Sandler [10,11] where, at equilibrium, the fugacity of water in the hydrate (H) phase is equated to the fugacity of water in the liquid phase(L). Mathematically, it can be written as

$$f_w^H = f_w^L \quad (1)$$

- **Hydrate Model (The fugacity of water in the hydrate phase)**

The fugacity of water in the hydrate phase is expressed in terms of potential differences, as proposed by VdWP theory [8], using the following equation:

$$f_w^H = f_w^\beta \exp\left(\frac{-\Delta\mu_w^H}{RT}\right) \quad (2)$$

$\Delta\mu_w^H$ is The difference between the chemical potential of water in the hypothetical and real (filled) hydrate phases and f_w^β is the fugacity of the hypothetical empty hydrate lattice and it is expressed by the following relation:

$$f_w^\beta = P_w^{sat,\beta} \phi_w^{sat,\beta} \exp\left[\frac{V_w^\beta (P - P_w^{sat,\beta})}{RT}\right] \quad (3)$$

The values of the vapor pressure of the empty hydrate ($P_w^{sat,\beta}$) have been fitted to experimental data. The equation for the empty hydrate structure vapor pressures proposed by Sloan et al. [18] are:

$$P_w^{sat,\beta,I} = 0.1 \exp\left(17.440 - \frac{6003.9}{T}\right) \quad (4)$$

The hydrate phase molar volumes (V_w^β) in equation (3) depend on pressure, which is important for the Poynting correction and it is determined from the equations proposed by Klauda and Sandler [10]:

$$V_w^{\beta,I} / m^3 mol^{-1} = (11.835 + 2.217 \times 10^{-5}T + 2.242 \times 10^{-6}T^2)^3 \times \frac{10^{-30}N_A}{N_w^{\beta,I}} - 8.006 \times 10^{-9}P(MPa) + 5.448 \times 10^{-12}P^2(MPa) \quad (5)$$

In Eqs. 5, N_A is the Avogadro's number and N_w^β is the number of water molecules in a unit cell ($N_w^{\beta,I} = 46$).

The difference in chemical potential of water between a theoretical empty hydrate water lattice (empty cavities) and the actual hydrate may be described by the presence of guest molecules in the water cavities, according to Langmuir adsorption theory.

$$\Delta\mu_w^H = -RT \sum_m v_m \ln(1 - \sum_{k=1}^N \theta_{mj}) \quad (6)$$



The term on the right side of the equation describes the stabilization of the unstable water lattice by the presence of guest molecules within the water cavities. v_m is the number of linked cavities per water molecule in the basic hydrate ($v_{small} = 1/23, v_{Large} = 3/23$ for structure I). θ_{mj} is the fractional occupancy of component j in cavity type m . This occupancy is described by:

$$\theta_{mj} = \frac{C_{mj}f_j}{1 + \sum_l C_{ml}f_l} \quad (7)$$

Where f_j is the fugacity of component j and C_{mj} is the temperature-dependent adsorption constant. Using the Lennard-Jones-Devonshire cell theory, van der Waals and Platteeuw showed that the Langmuir constant is:

$$C_{ki} = \frac{4\pi}{kT} \int_0^\infty \exp\left(-\frac{w(r)}{kT}\right) r^2 dr \quad (8)$$

Where T the absolute temperature, k is Boltzmann's constant and $w(r)$ is the interaction potential between the cavity and the gas molecule according to the distance r between the guest molecule and the water molecules over the structure. However, in the temperature range 260-300°K, the Langmuir constants can be calculated with the empirical relation using the following equation where A_{mj} and B_{mj} are constants (Table 1).

$$C_{mj} = \frac{A_{mj}}{T} \exp\left(\frac{B_{mj}}{T}\right) \quad (9)$$

Table 1. Langmuir constants for CO₂ and N₂ hydrates between 260 K and 300 K at structure I in equation 9 [9].

Component	Small cavity		Large cavity	
	$A_{mj} \times 10^3$ (K)	$B_{mj} \times 10^{-3}$ (K)	$A_{mj} \times 10^2$ (K)	$B_{mj} \times 10^{-3}$ (K)
CO ₂	1.1978	2.8605	0.8507	3.2779
N ₂	3.8087	2.2055	1.8420	2.3013

• **Fluid phase model (The fugacity of water in the Liquid phase)**

The expressions for the fugacity of water in the liquid phase is expressed using the following equation

$$f_w^L = P_w^{sat,L} x_w \gamma_w \phi_w^{sat,L} \exp\left[\frac{V_w^L(P - P_w^{sat,L})}{RT}\right] \quad (10)$$

The fugacity coefficient, $\phi_w^{sat,L}$, is taken to be unity because the vapor pressures of the water phases are low. For liquid water, the vapor pressure as a function of the temperature and molar volumes as a function of the temperature and pressure are determined from the Eqs. (11) and (12) as given by Klauda and Sandler [10].

$$\ln P_w^{sat,L} (Pa) = 4.1539 \ln T - \frac{5500.9332}{T} + 7.6537 - 16.1277 \times 10^{-3} T \quad (11)$$

$$\ln(V_w^L/m^3 mol^{-1}) = -10.9241 + 2.5 \times 10^{-4}(T - 273.15) - 3.53 \times 10^{-4}(P/MPa - 0.101325) + 1.559 \times 10^{-7}(P/MPa - 0.101325)^2 \quad (12)$$

The solubility of CO₂ and N₂ in water is low; however, at very high pressures this solubility cannot be assumed to be negligible. Therefore, to be consistent, the solubility of all guest compounds in water were calculated from

$$x_i = \frac{f_i^v}{H_i \exp\left(\frac{V_i^L(P - P_w^{sat})}{RT}\right)} \quad (13)$$

The volume of water in the Poynting correction in the above equations does depend on pressure, but because the change is small, we have assumed it to be constant ($V_{CO_2}^L = 33.9 \frac{cm^3}{mol}$ and $V_{N_2}^L = 35.7 \frac{cm^3}{mol}$ [31]). The Henry's constants are expressed using the mathematical equation below with constants (A, B, C and D) listed in Table 2.



$$-\ln \left[\frac{H_i/Pa}{101325} \right] = A + \frac{B}{T} + C \ln T + DT \quad (14)$$

Table 2 .Henry Law constants for CO₂ and N₂ [10]

Component	A(Pa)	B(Pa.K)	C(Pa)	D (Pa.K ⁻¹)
CO ₂	-159.8680	8742.426	21.6712	-0.00110
N ₂	-164.9970	8433.619	21.5601	0.00844

• **Gas-phase model (The fugacity of gas in the vapor phase)**

The fugacity of the components in the vapor phase is needed for calculation of the fugacity of water in the hydrate phase and liquid phase. The fugacity of the hydrate former f_j is given by:

$$f_j = \phi_j y_j P \quad (15)$$

ϕ_j is the fugacity coefficient of component j in the coexisting vapor phase and y_j is the mole fraction of component j in the vapor phase. For determination of the fugacity of the component of gas in the vapor phase, four cubic EOSs are included in this study: SRK, PR, PT, VPT.

For mixtures (as nonpolar components), the equation of state are widely applied to utilize the *van der Waals* mixing rules (known as the classical quadratic mixing rules) as follows:

$$a_{mix} = \sum_i \sum_j x_i x_j a_i^{0.5} a_j^{0.5} (1 - k_{ij}) \quad b_{mix} = \sum_i x_i b_i \quad c_{mix} = \sum_i x_i c_i \quad (16)$$

k_{ij} is called the binary interaction parameter. This parameter takes into account the attractive interaction between components and the fact that these interactions are different between each other (Table 3). The fugacity Coefficient of each component in liquid phases is calculated with the above EoS and the associated mixing rules.

Table 3. Binary interaction parameters for the CPA EOS [32,33]

EoS	PR	SRK	PT	VPT
k_{ij}	-0.007	-0.014	1.043	-0.036

Results and discussion

The proposed model was used to calculate the equilibrium pressures of pure CO₂ and simulated flue gas using the fugacity based approach of Klauda and Sandler [10, 11]. Four different EOS, viz., PR, SRK, PT and VPT had been used for calculating the fugacity of the gas component in the vapor phase.

The modeling results were compared with experimental data from the literature. Figures 1 and 2 show the model predicted equilibrium pressure versus temperature for pure CO₂ and simulated flue gas respectively. Also, the average absolute deviation percentage (AAD) between the experimental and thermodynamic model results (according to equation 12) for pure CO₂ and simulated flue gas for different moles Fraction of carbon dioxide are reported in Tables 4 and 5.

$$AAD\% = \frac{1}{NP} \sum_{i=1}^{NP} \frac{P_{exp} - P_{cal}}{P_{exp}} \times 100 \quad (12)$$

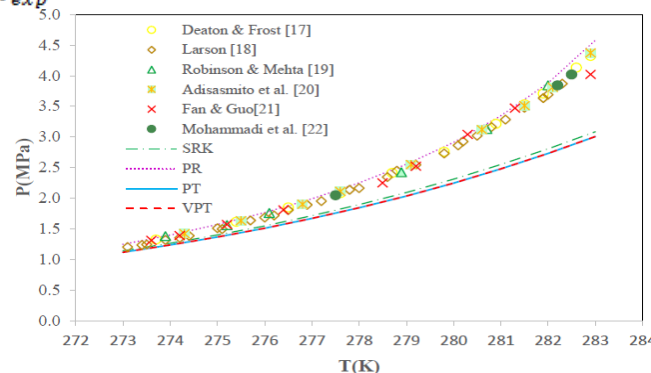


Fig. 1. Phase diagrams (P vs. T) of the clathrate hydrates of pure CO₂

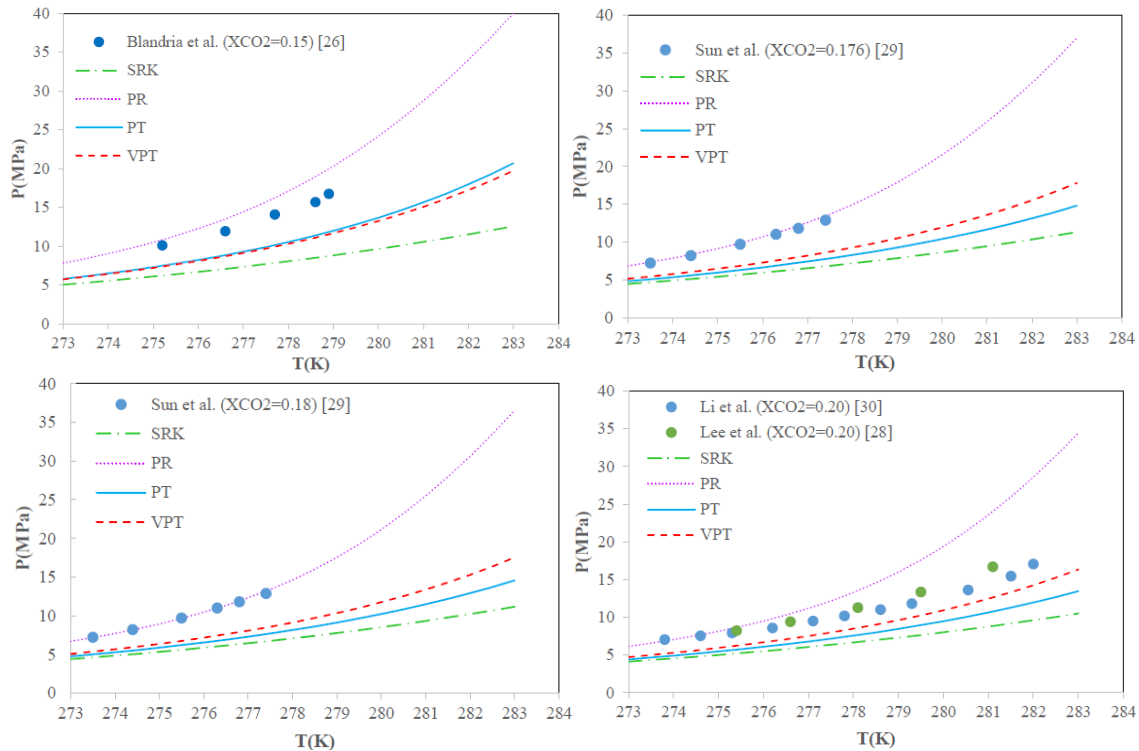


Fig. 2. Phase diagrams (P vs. T) of the clathrate hydrates of simulated flue gas

For pure carbon dioxide, the deviation of the predicted equilibrium pressure from the experimental data is less than 10 % in the temperature range 273 to 276. As the temperature rises, the value of average absolute deviation percentage increases. From Table 4, it can be seen that the minimum average absolute deviation of the predicted equilibrium pressure from the experimental is about 3.3 % for PR EOS. The estimates of equilibrium pressure for the CO₂ hydrates from the PT and VPT EOS have similar results (AAD = 17.4%).

In the case of the CO₂ and N₂ mixture hydrate, the pressure predicted by SRK EOS is high (about 38.66 %). However, the estimates of equilibrium pressure from the PR and VPT EOS are better than the values obtained from the SRK and PT EOS (AAD= 22.03 and 23.88 % respectively).

Table 4. Average absolute relative deviations, AAD%, of CO₂ hydrate formation equilibrium pressure

Researcher	Temperature Range (K)	Number of data point	(AAD%)			
			PR	SRK	PT	VPT
Deaton & Frost [17]	273.7-282.9	12	2.43	17.67	19.79	19.79
Larson [18]	273.1-282.3	30	4.13	13.18	15.40	15.40
Robinson & Mehta [19]	273.9-282.0	6	2.04	15.20	17.35	17.35
Adisasmito et al. [20]	274.3-282.9	9	2.09	17.97	20.10	20.10
Fan & Guo [21]	273.6-282.9	9	3.59	14.66	16.82	16.82
Mohammadi et al. [22]	277.5-282.5	3	3.97	21.47	23.55	23.56
Average	273-283	69	3.3	15.32	17.48	17.49



Table 5. Average absolute relative deviations, AAD%, of simulated flue gas mixture hydrate formation equilibrium pressure

Researcher	CO ₂ mole fraction	Temperature Range (K)	Number of data point	(AAD%)			
				PR	SRK	PT	VPT
Kang et al. [23]	0.176	272.85-280.55	5	30	37	28	20
Linga et al. [24]	0.169	273.7	1	2	36	30	25
Bruusgaard et al. [25]	0.17-0.183	275.3-281.1	6	46	33	22	12
Blandria et al. [26]	0.151	275.2-278.9	5	14	45	36	29
Darbonia et al. [27]	0.17	273.7	1	7	32	26	21
Lee et al. [28]	0.20	275.4-281.1	5	22	41	23	24
Sun et al. [29]	0.18	273.5-277.4	6	1	43	36	31
Li et al. [30]	0.202	273.8-282	11	30	38	29	20
Average	0.151-0.202	272.85-282	40	23.88	38.66	30.01	22.03

Conclusion

A thermodynamic model was presented based on Claude and Sandler for the predicting three phases equilibria combined with the different Equation of State (PR, SRK, PT and VPT) for pure CO₂ and simulated flue gas at temperature range of 273–283 K. The results of model were compared to the available data from the experimental literature.

For the pure CO₂ results showed that the average absolute deviation percentage between the experimental and thermodynamic models results increased with an increase in the temperature for all EOS. Also, the equilibrium pressures obtained from the model have good agreements with experimental data for an AAD approximately to 3.3 % by PR EOS. The estimates of equilibrium pressure for the CO₂ hydrates from the PT and VPT EOS had similar results (AAD=17.4%). In the case of the SRK EOS, the average absolute deviation percentage was obtained about 15.30.

For simulated flue gas system, the equilibrium pressures obtained by SRK EOS had maximum deviation (AAD=38.66%) from the experimental data, whereas the minimum deviation was 22.03 % for VPT EOS. Also the average absolute deviation percentage from PR and PT EOS was obtained 23.88 and 30.01 respectively.

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