

## PREDICTION OF GAS HYDRATE PHASE BEHAVIOR WITH PRSV2 EQUATION OF STATE

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### ABSTRACT

In this paper, a simple thermodynamic model is developed to calculate the phase equilibrium of pure gas hydrates ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ). The equality of fugacity approach is used to model the vapor-liquid-hydrate phase equilibrium. The van der Waals and Platteuw model is applied to describe the hydrate phase, and PRSV2 EOS with Van Laar-type two-binary-parameter mixing rule is chosen to calculate the fugacities of vapor and liquid phases. The model parameters are fitted to experimental data for pure gas hydrate, and this model is able to precisely predict vapor-liquid-hydrate forming pressure for single guest hydrate.

### NOMENCLATURE

#### Roman Characters

$a$  = attractive parameter in PRSV2 EOS

$b$  = volume parameter in PRSV2 EOS

$A_{ml}$  = Langmuir constant parameter

$B_{ml}$  = Langmuir constant parameter

$C$  = Langmuir constant

$f$  = fugacity

$k_{ij}$  = binary interaction parameter

$k$  = Boltzmann constant

$N_{data}$  = number of data

$r$  = radial distance

$P$  = pressure

$R$  = gas constant

$R(cell)$  = cell radius

$T$  = temperature

$v$  = molar volume

$W(r)$  = cell potential

$x$  = molar composition

#### Superscripts and Subscripts

$H$  = hydrate phase

$L$  = liquid phase

$l$  = guest

$m$  = cage type

$V$  = vapor phase

$w$  = water

Greek characters

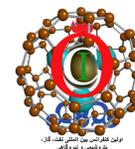
$\beta$  = empty hydrate phase

$\phi$  = fugacity coefficient

### INTRODUCTION

Gas hydrates are ice-like crystalline solids that consist water and usually smaller gas guest e.g.  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , which usually form under high pressure and low temperature environment. The water molecules constitute cage-like crystal lattice due to hydrogen bonding, and the lattice is stabilized by encapsulating of gas molecules. There are three mainly structure for gas hydrates: structure I (sI) structure II (sII), and structure H (sH) [1]. To understand the phase behavior and stability of gas hydrates in the large range of temperature and pressure, an accurate thermodynamic model is necessary.

Many thermodynamic model for phase equilibrium in the hydrate system had been reviewed and discussed [1, 2-3]. van der Waals and Platteuw derived the basic statistic thermodynamic model with Leonard-Jones potential function to calculate pure gas hydrate dissociation pressure in 1959, and most of models for the hydrate phase are based on vdWP model [4]. In 1972, Parrish and Prausnitz used vdWP model with Kihara potential to extend the vdWP model in calculating phase equilibria for single and mixed gas hydrates [5]. In the vdWP, the equilibrium criteria is that the chemical potential of water in different phases must be equal, and there are many reference energy parameters should be regressed to evaluate fugacity in the hydrate phase. To avoid this



problem, the fugacity-based approach for modeling hydrate-liquid-vapor ( $H-L_w-V$ ) phase equilibrium was expanded. Chen and Guo used fugacity approach in the vdWP model, and evaluate the fugacities in the fluid phases by Patel-Teja (PT) EOS [6-7]. Klauuda and sandler also presented the fugacity approach model. They used the PRSV EOS in the vapor phase, and modeled the liquid phase by Henry's law correlation and modified UNIFAC [8]. In Klauuda's model, the Kihara potential parameters were based on Tse et al. [9] and there are three parameters fitted by pure gas hydrate experimental data for reference fugacity in the empty hydrate phase. Zhang followed Klauuda's fugacity approach, and only used two adjustable parameters in their model to evaluate the equilibrium pressure for single gas hydrate system below 300 K, and using the PRSV EOS to model both liquid and hydrocarbon phases [10]. In 2011, Bandyopadhyay and Klauuda used PSRK EOS to describe the fugacity of non-hydrate phases that in equilibrium with gas hydrates, but the fugacity of water in the liquid phase was modified of obtaining from PSRK EOS directly [11].

In this paper, we use PRSV2 EOS coupled with Van Laar-type two-binary-parameter mixing rule to model both liquid and vapor phases instead of using different models in these two phases. Experimental VLE data for all system were extracted from literature [15-18], then by using these experimental data and the method of algorithm genetic the best fitted interaction parameters have been found in different temperatures in such a way that the minimum deviations from experimental data have been raised. In the next step, these interaction parameters have been fitted in terms of temperature. The fugacity of water in the hydrate phase was described by the vdWP model, however the Langmuir constant are expressed as a function of temperature instead that calculated by potential function. There are two to four parameters in evaluating the Langmuir constant, and the parameters are regressed by pure gas hydrate equilibrium data. This model use the basic EOS and mixing rule with modified vdWP model and give good accuracy in  $H-L_w-V$  phase equilibrium for pure gas hydrate.

## THERMODYNAMIC MODEL

### Component fugacity in fluid phases

In order to give correct description of the hydrate phase, the phase behavior of non-hydrate phases at equilibrium is important. Previous work for  $H-L_w-V$  phase modeling [7,9,12] used cubic EOS to model the vapor phase and chosen liquid model to describe the liquid phase. To simplify the thermodynamic model in this work, a single EOS is used to describe both vapor and liquid phases. The PRSV2 EOS modified from Peng-Robinson EOS is used in this work [13-14]:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2vb - b^2} \quad (1)$$

where  $P$  and  $T$  is the pressure and temperature,  $R$  is gas constant, and  $a$  and  $b$  are attractive parameter and volume parameter in PRSV2 EOS. There is an added adjustable characteristic parameters,  $k_1, k_2, k_3$ , of each compound in PRSV2 EOS in order to modify original PR EOS, and  $k_1, k_2, k_3$  of components in this paper are from Stryjek and Vera [13-14].

Each system included in this study contains two compound, so the PRSV2 EOS must be combined with the mixing rule for mixture. In this paper, we use the Van Laar-type two-binary-parameter mixing rule to obtain parameters in PRSV2 EOS for mixture. The parameters  $a$  and  $b$  in PRSV2 eos evaluated by Van Laar-type two-binary-parameter mixing rule are given by

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (2)$$

$$b_m = \sum_i x_i b_i \quad (3)$$

$$a_{ij} = \sqrt{a_i a_j} \left( 1 - \frac{k_{ji} k_{ij}}{x_i k_{ij} + x_j k_{ji}} \right) \quad (4)$$



where  $a_i$  and  $b_i$  are pure parameters and  $a_m$ ,  $b_m$  are parameters of mixture in PRSV2 EOS. The  $k_{ij}$  and  $k_{ji}$  are the binary interaction parameters. In this paper experimental VLE data for systems were extracted from literature, then by using these experimental data and the method of algorithm genetic the best fitted interaction parameters have been found in different temperatures in such a way that the minimum deviations from experimental data have been raised. In the next step, these interaction parameters have been fitted in terms of temperature. Table 1 shows the binary interaction parameters between water and guest component as a function of temperature according to the following equation:

$$k_{ij} = q_{ij}T + p_{ij} \quad (5)$$

$$k_{ji} = q_{ji}T + p_{ji} \quad (6)$$

Table 1  
Binary interaction parameters for PRSV2 EOS

| $i$                           | $j$              | $q_{ij}$ | $p_{ij}$ | $q_{ji}$ | $p_{ji}$ |
|-------------------------------|------------------|----------|----------|----------|----------|
| CH <sub>4</sub>               | H <sub>2</sub> O | 0.0035   | -0.65    | 0.0025   | -0.72    |
| C <sub>2</sub> H <sub>6</sub> | H <sub>2</sub> O | 0.0014   | -0.81    | 0.0034   | -0.74    |
| C <sub>3</sub> H <sub>8</sub> | H <sub>2</sub> O | 0.0003   | -0.55    | 0.0023   | -0.36    |
| i-C <sub>4</sub>              | H <sub>2</sub> O | 0.001    | -0.07    | 0.0017   | 0        |
| N <sub>2</sub>                | H <sub>2</sub> O | 0.0039   | -0.2     | 0.0035   | 0.65     |
| CO <sub>2</sub>               | H <sub>2</sub> O | 0.0051   | -0.14    | 0.0047   | -0.32    |

#### Water fugacity in hydrate phase

The model for the hydrate phase is based on the vdWP model [4], and used fugacity approach to evaluate the water fugacity in the hydrate phase. The fugacity of water in the hydrate phase is as follows:

$$f_w^H(T, P) = f_w^\beta(T, P) \cdot \exp\left(\sum_m v_m \ln\left(1 - \frac{C_{ml}(T)f_l(T, P, \underline{y})}{1 + \sum_l C_{ml}(T)f_l(T, P, \underline{y})}\right)\right) \quad (7)$$

where  $f_l$  is the fugacity of the gas component in the vapor phase, and  $f_w^\beta$  is the fugacity of hypothetical empty hydrate lattice and given by:

$$f_w^\beta = P_w^{sat, \beta} \phi_w^{sat, \beta} \exp\left(\frac{\int_{P_w^{sat, \beta}}^P V_w^\beta(T, P) dP}{RT}\right) \quad (8)$$

where the saturated vapor pressure of empty hydrate  $P_w^{sat, \beta}$  correlated is as followed: for sI

$$\ln P_w^{sat, \beta} = 17.44 - \frac{6003.9}{T} \quad (9)$$

for sII

$$\ln P_w^{sat, \beta} = 17.332 - \frac{6017.6}{T} \quad (10)$$

$\phi_w^{sat, \beta}$  is the fugacity coefficient of water in the empty hydrate lattice, and it is assumed to be unity because the vapor pressure of water in the solid phase is low.  $V_w^\beta(T, P)$ , is the molar volume of the empty lattice, depends on temperature and pressure, and it is given by Klauda and Sandler [8]. In equation (7),  $v_m$  is the number of cages of type  $m$  per water molecules in the hydrate lattice.  $C_{ml}(T)$  is the Langmuir constant for guest gas  $l$  in type  $m$  cage. In the Parrish and Prausnitz model [5],  $C_{ml}(T)$  is expressed as:

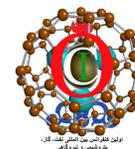
$$C_{ml}(T) = \frac{4\pi}{kT} \int_0^{R(cell)} \exp\left(\frac{W(r)}{kT}\right) r^2 dr \quad (11)$$

where  $A_{ml}$  and  $B_{ml}$  are the fitting parameters and obtained by data regression of experimental phase equilibrium pressure of pure gas hydrates, e.g. methane hydrate, and there are two to four adjustable parameters in this model.

#### Phase equilibrium criteria

The classical thermodynamic fugacity approach is used in this work to model hydrate-liquid-vapor phase equilibrium. At equilibrium, the fugacity of water in vapor ( $V$ ), liquid water ( $L$ ), and hydrate phase ( $H$ ) is equal at temperature  $T$  and pressure  $P$ :

$$f_w^V(T, P, \underline{y}) = f_w^L(T, P, \underline{x}) = f_w^H(T, P) \quad (12)$$



where  $y$  and  $x$  is the molar composition in the vapor and liquid phase.

## RESULTS AND DISCUSSION

The comparison between the results from this model and experimental data is defined by average absolute deviation (AAD). The average absolute deviation in pressure (AADP) are defined as follows:

$$AADP(\%) = \frac{100}{N_{data}} \sum_{i=1}^{N_{data}} \left| \frac{p_i^{exp} - p_i^{model}}{p_i^{exp}} \right| \quad (13)$$

where  $N_{data}$  is the number of data points.

### Single gas hydrate results

To calculate the single gas hydrate equilibrium, the Langmuir constant in equation (12) need to be regressed from experimental phase equilibrium data [1]. Table 2 shows the Langmuir constant parameters for six guest hydrates. It is well understood that the  $CH_4$  and  $CO_2$  molecules is small enough to be trapped either in the large cage or in the small cage of the sl. Thus, there are two Langmuir constant parameters  $A_{ml}$  and  $B_{ml}$  for each (small or large) cage. The  $C_2H_6 + H_2O$  hydrate system has a very little occupation for small cage and the  $C_3H_8$  molecule is too large to be trapped in the small cage, thus, ethane and propane molecule have only two parameters.

The results for calculating  $H-L_w-V$  phase equilibrium for single gas hydrate by this model are compared to Sloan's model [1], and two fugacity approach model (Zhang et al. [10] and Klauda [11]) in Table 3. The number of fitting parameters in our model is two or four, and there are two and three fitting parameters in respectively, Zhang's and Klauda's work. And we assume that the Langmuir constant is only temperature – dependent and use an exponential form instead of potential function to describe Langmuir constant. It has been found that our model can give consistent results with experimental data. Fig 1 to Fig 6 shows that the model can well describe the variation of pressure as a function of temperature for the  $H-L_w-V$  phase equilibrium of all the system. For all system, the average absolute deviations in pressure (AADPs) obtained by this model are smallest

among three compared papers for temperature range.

Table 2  
Langmuir constant parameters for pure gas hydrate

| Guest    | Structure | Large cage          |                 | Small cage          |                 |
|----------|-----------|---------------------|-----------------|---------------------|-----------------|
|          |           | $A_{ml}$<br>(K/KPa) | $B_{ml}$<br>(K) | $A_{ml}$<br>(K/KPa) | $B_{ml}$<br>(K) |
| $CH_4$   | I         | 0.215               | 2731            | 0.00683             | 2806            |
| $C_2H_6$ | I         | 0.0331              | 3914            | -                   | -               |
| $C_3H_8$ | II        | 0.0498              | 4783            | -                   | -               |
| $CO_2$   | I         | 0.397               | 2746            | 0.0028              | 3365            |
| $N_2$    | II        | 0.0573              | 2559            | 0.01956             | 2845            |

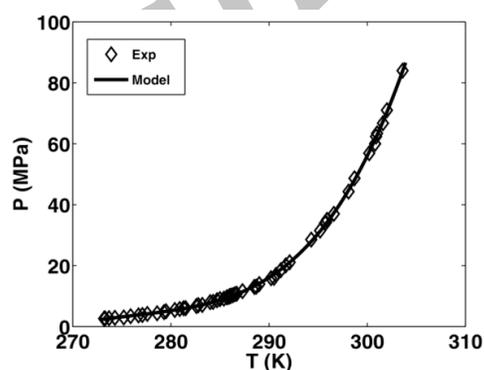


Fig 1  
Phase equilibrium of methane

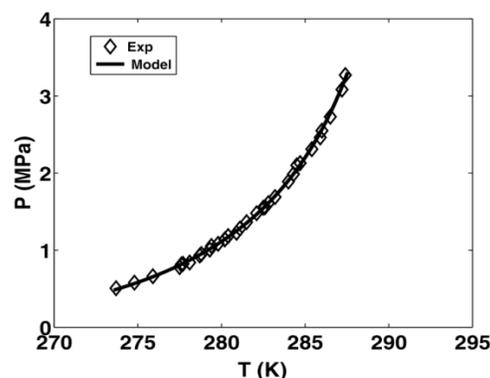


Fig 2  
Phase equilibrium of ethane

In this work, the accuracy of  $CO_2$  system is slightly worse than the Zhang model, and this model can perform well in the  $CH_4$  system above 300 K.

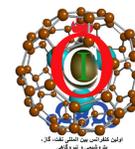


Table 3  
Comparison pure gas hydrate equilibrium prediction results (Experimental data are from Sloan [1])

| Guest                         | Equilibria                | Data pts. | Temp. range<br>(K) | %AADP from experimental data |       |        |           |
|-------------------------------|---------------------------|-----------|--------------------|------------------------------|-------|--------|-----------|
|                               |                           |           |                    | Sloan                        | Zhang | Klauda | This work |
| CH <sub>4</sub>               | H(SI)-L <sub>w</sub> - V  | 90        | 273.2-303.6        | 3.44                         | 2.83  | 2.65   | 2.15      |
| C <sub>2</sub> H <sub>6</sub> | H(SI)-L <sub>w</sub> - V  | 51        | 273.4-287.4        | 10.94                        | 3.04  | 3.51   | 2.97      |
| C <sub>3</sub> H <sub>8</sub> | H(SII)-L <sub>w</sub> - V | 51        | 273.2-278.2        | 3.32                         | 2.99  | 3.41   | 3.22      |
| CO <sub>2</sub>               | H(SI)-L <sub>w</sub> - V  | 115       | 271.6-282.8        | 3.22                         | 1.04  | 2.79   | 1.17      |
| N <sub>2</sub>                | H(SII)-L <sub>w</sub> - V | 56        | 272-299.6          | 4.3                          | 3.61  | 9.28   | 2.21      |

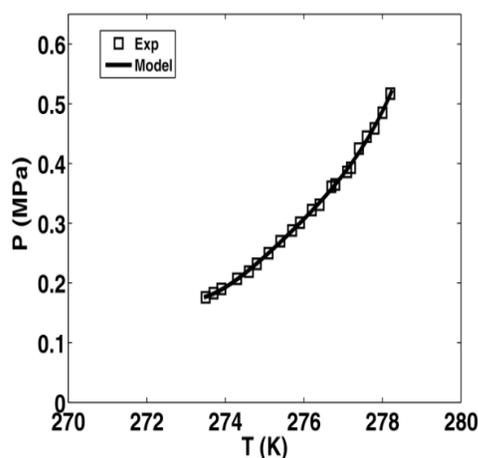


Fig 3  
Phase equilibrium of propane

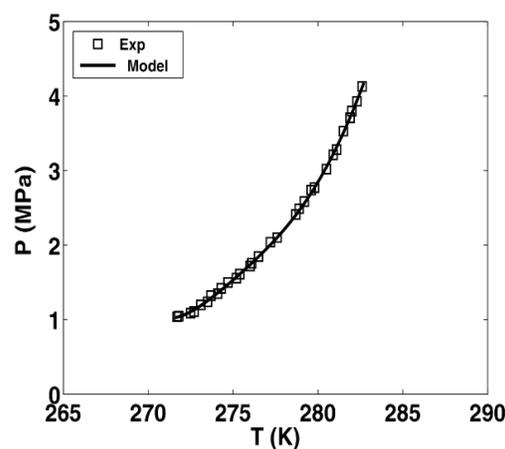


Fig 5  
Phase equilibrium of carbon dioxide

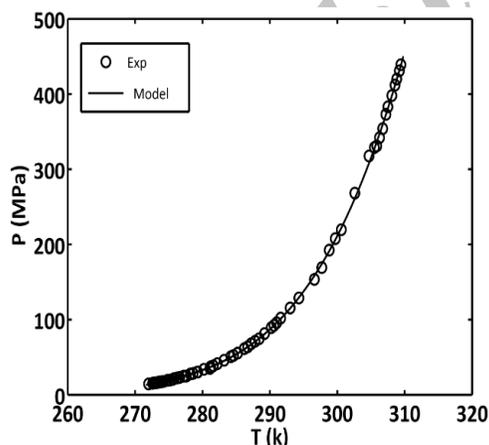


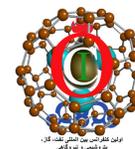
Fig 4  
Phase equilibrium of nitrogen

## CONCLUSION

In this paper, a simple model is proposed to accurately calculate vapor – liquid – hydrate phase equilibrium for pure gas hydrates. The model is composed of the PRSV2 EOS, the Van Laar – type two – binary – parameter mixing rule and the vdWP model. Instead of using a complicated energy function to describe the Langmuir constants in the vdWP model, there are only two or four fitting parameters in the systems to determine the temperature – dependent Langmuir constant, and these model parameters are used directly in giving prediction in hydrate systems. This simple model can well describe the phase behavior of vapor – liquid – hydrate phase equilibrium for pure gas hydrates.

## KEYWORDS

Gas hydrate, PRSV2 EOS, vdWP model, Mixing- rule, Algorithm genetic



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