

Prediction of Gas Hydrate Forming Pressures by Using PR Equation of State and Different Mixing Rules

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Abstract

In this work, the ability of different mixing rules for the prediction of hydrate formation pressure are compared. For this purpose, by using Van der Waals–Platteeuw model for solid hydrate phase and PR equation of state for calculation of fugacity of components in gas and liquid phases, the pressure of hydrate formation in different mixtures has been calculated by four different mixing rules: Van der Waals, Danesh, GNQ and Wong-Sandler, then by comparison of the calculated results with experimental data, the accuracy of the mixing rules were determined. Studied systems contain binary mixtures CH₄, C₂H₆, C₃H₈, i-C₄H₁₀, CO₂, and H₂S with water in hydrate forming conditions. The interaction parameters in each mixture have been optimized by using two phase equilibrium data (VL_w) and then the optimized parameters have been used for three phase equilibrium (VL_wH) calculations. Comparison of the calculated pressure of hydrate forming with experimental pressure shows that for most mixtures in the studied temperature and pressure ranges, the GNQ mixing rule with an average percent of error 6% has more accuracy than the three other mixing rules: Van der Waals, Danesh and WS. According to the obtained results for methane equilibrium concentrations in liquid phase, it seems that Danesh mixing rule is more efficient for the prediction the mole concentrations of components. Since Danesh rule considers the polarity of the water molecule, it has greater precision in predicting the equilibrium fractions.

Keywords: *Mixing Rules, Peng-Robinson, Equation of State, Gas Hydrate, Three Phase Equilibria*

1- Introduction

Natural gas is one of the most important sources of energy in the world. One of the related problems to natural gas is gas hydrate formation. Gas hydrates are crystalline solids that form when gas or volatile liquid molecules suitable for hydrate formation are

enclosed in a cage consisting of water molecules. Naturally occurring hydrates, containing mostly methane, exist in vast quantities and are being looked upon as a potential alternative energy source. Carbon dioxide hydrates are also important hydrates [1].

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Although hydrate formation is referred to as an advantage, this circumstance in gas transportation lines causes some problems like plugging of the lines and sometimes the explosion of pipes. Thus awareness of equilibrium conditions of hydrate formation is necessary for preventing this event.

In this work, equilibrium conditions in hydrate formation for six mixtures that contain binary systems have been studied. (CH₄-H₂O), (C₂H₆-H₂O), (C₃H₈-H₂O), (i-C₄H₁₀-H₂O), (CO₂-H₂O) and (H₂S-H₂O). The forming pressure in each system was calculated.

2- Modeling

At phase equilibrium, the fugacities or chemical potentials of species in the various phases must be equal. For three-phase hydrate-liquid water-vapor, (VL_wH) equilibrium, the basic equations for the equilibrium condition are:

$$f_i^V = f_i^L = f_i^H \quad (1)$$

Calculation of component fugacities in two phases, vapor and liquid, are based on the ($\varphi - \varphi$) and ($\gamma - \varphi$) approach, and in this research the ($\varphi - \varphi$) model is used. In this method the fugacity of a component must be calculated using a suitable equation of state and mixing rules. In this study, Peng – Robinson equation of state was selected. The PR equation is [2]:

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

$$\begin{aligned} b &= 0.07780 \frac{RT_c}{P_c} \\ a &= 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T_r) \\ \alpha(T_r) &= \left(1 + m \left[1 - \left(\frac{T}{T_c} \right)^{0.5} \right] \right)^2 \\ m &= 0.37464 + 1.5422 \omega - 0.26922 \omega^2 \end{aligned} \quad (3)$$

The coefficients a , b of Eq (2) were obtained for mixtures using the Van der Waals, Danesh, GNQ (general non quadratic) and WS (Wong-Sandler) mixing rules. The Van der Waals mixing rule is:

$$\begin{aligned} a_{mix} &= \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j a_{ij} (1 - k_{ij}) \\ b_{mix} &= \sum_{i=1}^{NC} x_i b \end{aligned} \quad (4)$$

Where k_{ij} is the binary interaction parameter and:

$$a_{ij} = (a_i a_j)^{0.5} \quad (5)$$

In another applied mixing rule, the attraction parameter a has been separated into two parts, the Van der Waals classical mixing rule part a^C and the asymmetric contribution part a^A are as follows [3]:

$$a = a^C + a^A \quad (6)$$

$$a^A = \sum_{P=1}^{NPOLAR} x_P^2 \sum_{i=1}^{NC} x_i a_{Pi} l_{Pi} \quad (7)$$

p stands for polar component and l_{Pi} is the binary interaction parameter between the polar component and the other components, which is a function of temperature,

calculated by the following expression [3]:

$$l_{pi} = l_{pi}^0 - l_{pi}^1(T - T_0) \quad (8)$$

Where l_{pi}^0 and l_{pi}^1 are binary interaction parameters and T_0 is the ice point in K.

Another mixing rule used in this research is GNQ (general non quadratic) mixing rule. The general form in this rule for a_{mix} and b_{mix} parameters is the same as Van der Waals mixing rule, but the combining rule for a_{ij} has the following form [4]:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad , \quad k_{ij} = \delta_i x_i + \delta_j x_j \quad (9)$$

In the WS mixing rule, the molar excess Gibbs free energy at infinite pressure, calculated from an EOS, is equated to the same property calculated from the NRTL excess free energy model. The WS mixing rules are [5]:

$$b_{mix} = \frac{Q}{1 - D} \quad (10)$$

$$\frac{a_{mix}}{RT} = Q \times \frac{D}{1 - D} = D \times b_{mix} \quad (11)$$

$$D = \sum x_i \frac{a_i}{b_i RT} + \frac{g^E}{C^* RT} \quad (12)$$

$$Q = \sum \sum x_i x_j (b - \frac{a}{RT})_{ij} \quad (13)$$

$$(b - \frac{a}{RT})_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (14)$$

Where x_i is the mole fraction of component i in that phase and C^* is a constant depending on the EOS (where $C^* = -0.802$ for the PR EoS). The NRTL model was used for g^E .

$$\left(\frac{g^E}{RT} \right)_{NRTL} = \sum_i x_i \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \quad (15)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \quad (16)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (17)$$

The chemical potential of water in the hydrate phase is given by Van der Waals and Platteeuw [6]:

$$\begin{aligned} \frac{\Delta \mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{\beta-1/L}}{RT^2} dT + \int_{P_0}^P \frac{\Delta v_w^{\beta-1/L}}{RT} dP - \ln(\gamma_w x_w) \\ = \sum_{m=1}^{N_{cavity}} v_m \ln \left(1 + \sum_{j=1}^{NH} C_{jm} f_j \right) \end{aligned} \quad (18)$$

Where, v_m is the number of cavities of type m per water molecule in the lattice, C_{jm} is the Langmuir Constant, and f_i is the fugacity of the gas component i .

The Langmuir constants account for the gas-H₂O interaction in the cavity. Using the Lennard-Jones-Devonshire cell theory, Van der Waals and Platteeuw showed that the Langmuir constant is [7]:

$$C = \frac{4\pi}{kT} \int_0^R \exp\left(\frac{-\omega(r)}{KT}\right) r^2 dr \quad (19)$$

Where T is the absolute temperature, k is Boltzmann's constant and $w(r)$ is the

spherically symmetric cell potential which is a function of the cell radius, the coordination number and the nature of the gas-H₂O interaction. Usually the Kihara potential function with a spherical core for describing the interaction between the gas and water molecules in the cavity wall is used. Kihara parameters used in this work are given in Table (1) for the applied components.

Table 1. Kihara potential parameters [8]

component	a (°A)	σ (°A)	ε/k ($1/K$)
C1	0.295	3.2512	153.69
C2	0.488	3.4315	183.32
C3	0.730	3.4900	189.27
i-C4	0.798	3.6000	209.58
n-C4	1.029	3.4000	195.36
CO ₂	0.753	2.9040	171.97
H ₂ S	0.717	2.8770	210.50

3- Results and discussion

3.1- Results of optimization

For calculation pressure in equilibrium conditions using the ($\varphi - \varphi$) model, first we must determine the interaction parameters in

each mixing rule. These parameters are determined for each mixture by minimizing the following objective function:

$$O.F = w_1 \sum_{i=1}^{NP} \frac{|p_i^{cal} - p_i^{exp}|}{p_i^{exp}} + w_2 \sum_{i=1}^{NP} \frac{|x_i^{cal} - x_i^{exp}|}{x_i^{exp}} \quad (20)$$

Where w_1 and w_2 are the weight fraction in each term and $w_1 = w_2 = 1$.

Binary interaction parameter in the Van der Waals mixing rule is k_{12} , and this optimized value is given in Table (2). In the Danesh mixing rule, three parameters exist that contain k_{12} , l_{21}^0 and l_{21}^1 . The obtained parameters are presented in Table (3).

Tables (4) and (5) show the optimized values for GNQ and WS mixing rules respectively. In the GNQ mixing rule, δ_1 and δ_2 , and in the WS mixing rule, $g_{21} - g_{11}$, $g_{12} - g_{22}$, α_{12} , k_{12} are interaction parameters for binary mixtures.

Table 2. optimized parameters, k_{ij} , for Van der Waals mixing rule in PR EOS

Mixture	CH ₄ -H ₂ O	C ₂ H ₆ -H ₂ O	C ₃ H ₈ -H ₂ O	C ₄ H ₁₀ -H ₂ O	CO ₂ -H ₂ O	H ₂ S-H ₂ O
k_{12}	-0.35022	-0.22093	-0.25718	-0.31265	-0.14304	-0.02670

Table 3. optimized parameters, k_{ij} and l_{ij} for Danesh mixing rule in PR EOS

Mixture	k_{21}	l_{21}^0	$l_{21}^1 * 10^4$
CH ₄ -H ₂ O	0.48960	1.74473	71.181
C ₂ H ₆ -H ₂ O	0.49209	1.45850	37.830
C ₃ H ₈ -H ₂ O	0.52681	1.56193	36.518
i- C ₄ H ₁₀ -H ₂ O	0.34199	1.31380	49.953
CO ₂ -H ₂ O	0.25023	0.83331	24.882
H ₂ S-H ₂ O	0.13137	0.36095	14.224

Table 4. optimized parameters, δ_i for GNQ mixing rule in PR EOS

Mixture	δ_1	δ_2
CH ₄ -H ₂ O	0.16875	0.07576
C ₂ H ₆ -H ₂ O	0.36333	0.06920
C ₃ H ₈ -H ₂ O	0.45046	0.092116
i-C ₄ H ₁₀ -H ₂ O	1.07940	0.11403
CO ₂ -H ₂ O	0.02552	0.05083
H ₂ S-H ₂ O	0.03256	0.01187

Table 5. optimized parameters for WS mixing rule in PR EOS

Mixture	$g_{21} - g_{11}$	$g_{12} - g_{22}$	α_{12}	k_{12}
CH ₄ -H ₂ O	60.1736	23938.7640	0.70966	3.27553
C ₂ H ₆ -H ₂ O	-1010.2922	137.0329	0.62357	3.77522
C ₃ H ₈ -H ₂ O	293.4141	15766.5426	0.27138	3.29269
C ₄ H ₁₀ -H ₂ O	285.3414	5888.9290	0.27696	3.29248
CO ₂ -H ₂ O	318.1248	14875.8500	0.39698	1.52926
H ₂ S-H ₂ O	137.1430	30296.7154	-0.17181	1.16000

3.2- Results of equilibrium calculation

Fig. 1 shows the equilibrium curve for the predicted methane hydrate formation pressure based on different mixing rules. Error of calculated pressure in the PR equation of state by using the Danesh mixing rule, Van der Waals, GNQ and WS respectively is 11.62%, 13.16%, 16.74% and 12.33%. So Danesh mixing has a minimum of error for methane hydrate in PR EOS. The reason for the high error in methane hydrate is high formation pressure. The error percent of the model increases at high pressures.

As shown in Fig. 1, the obtained results of GNQ mixing rule has considerable deviation

with the experimental data at high temperatures.

Model predictions of methane solubility in liquid water for temperatures between 262.4 and 320.1 K and for pressures between 17.9 and 3970 bar are presented in Fig. (2). Danesh mixing with 7.32% error has more accuracy than the three other mixing rules.

Results of three phase equilibrium calculation (VL_wH) for other systems are given in Figs. 3 to 7. These figures show the predicted values of ethane, propane, carbon dioxide and hydrogen sulfide hydrates formation temperatures, respectively.

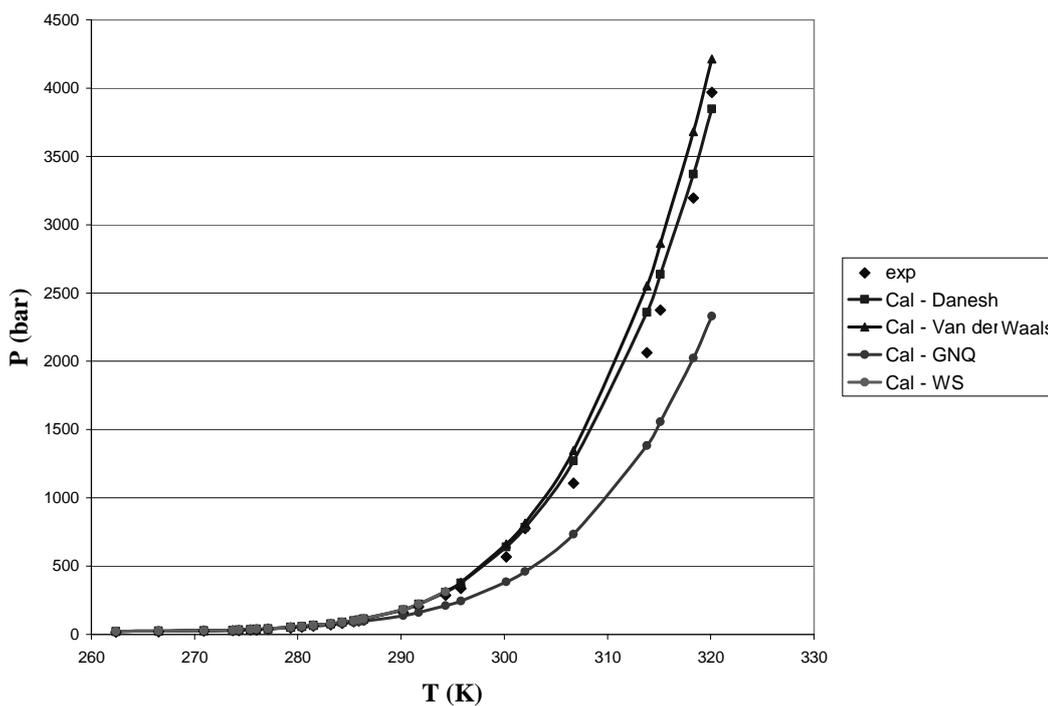


Figure 1. three phase equilibrium curve of methane hydrate based on four mixing rules by using PR equation of state

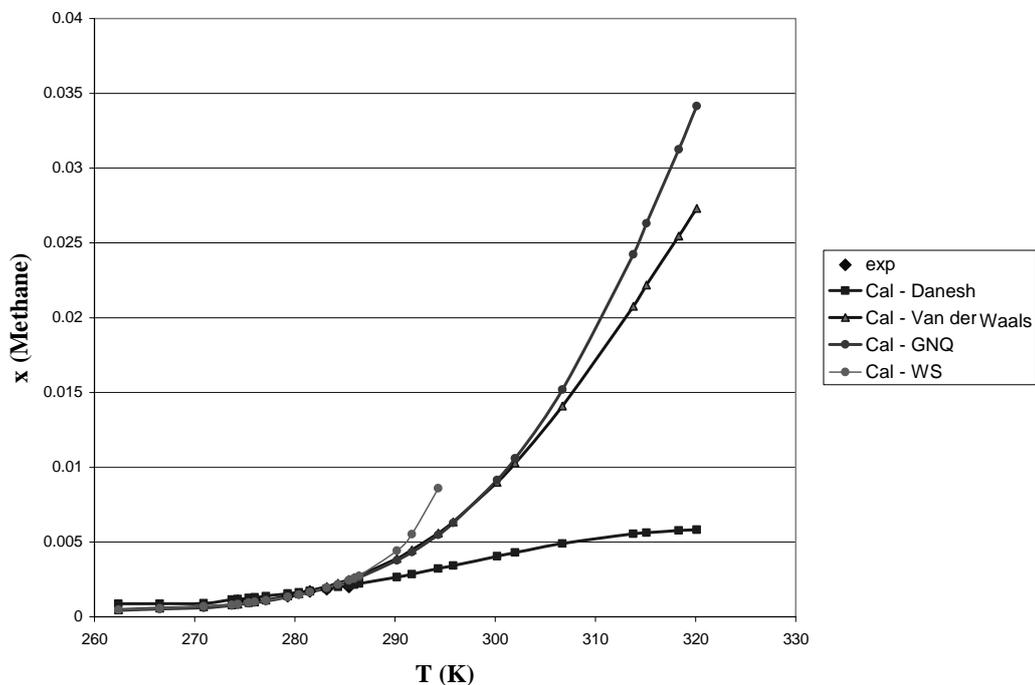


Figure 2. Comparison of calculated methane solubility in liquid water by using PR EOS and four mixing rules, with experimental data

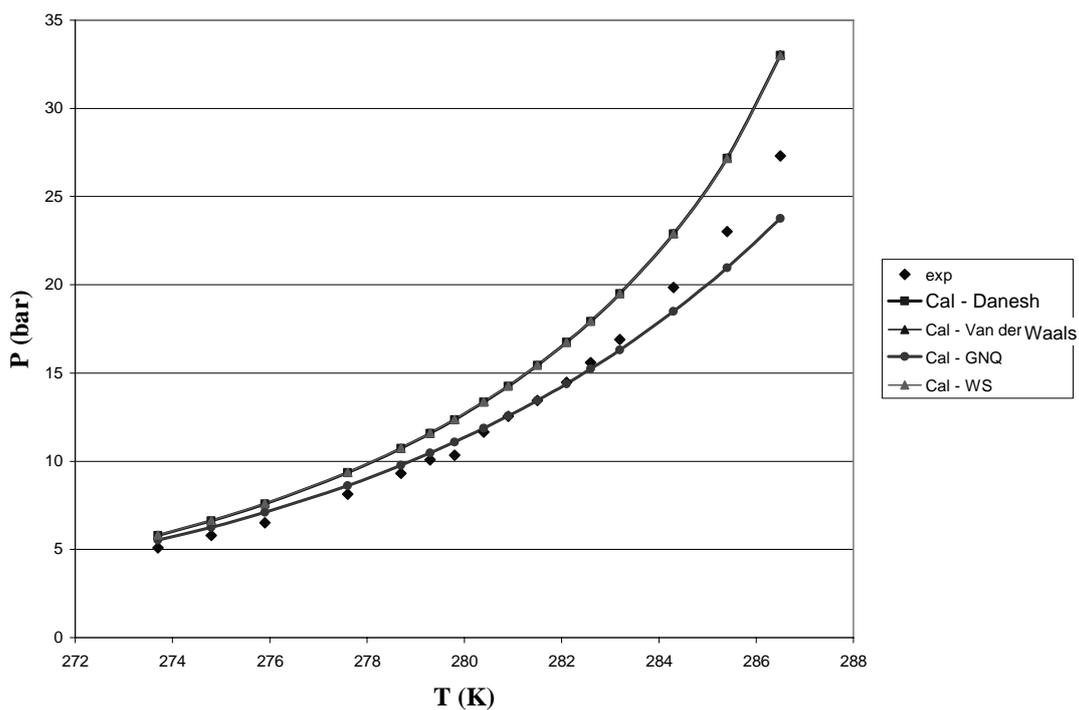


Figure 3. three phase equilibrium curve of ethane hydrate based on four mixing rules by using PR equation of state

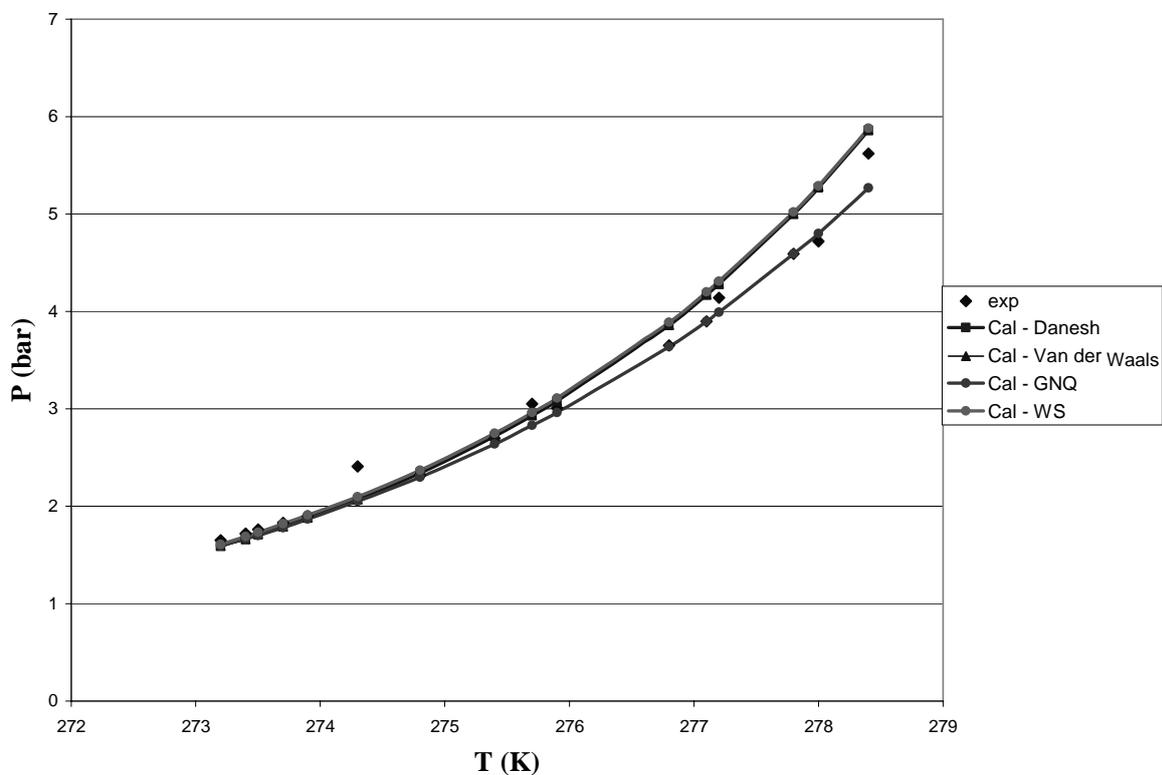


Figure 4. three phase equilibrium curve of propane hydrate based on four mixing rules by using PR equation of state

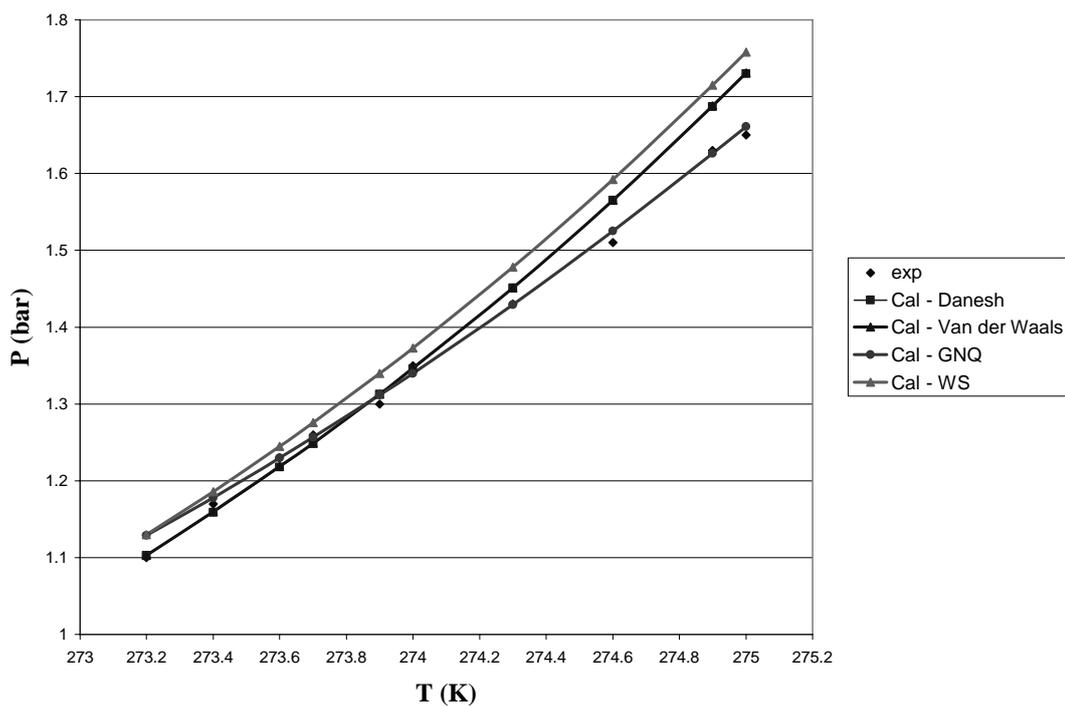


Figure 5. three phase equilibrium curve of i-butane hydrate based on four mixing rules by using PR equation of state

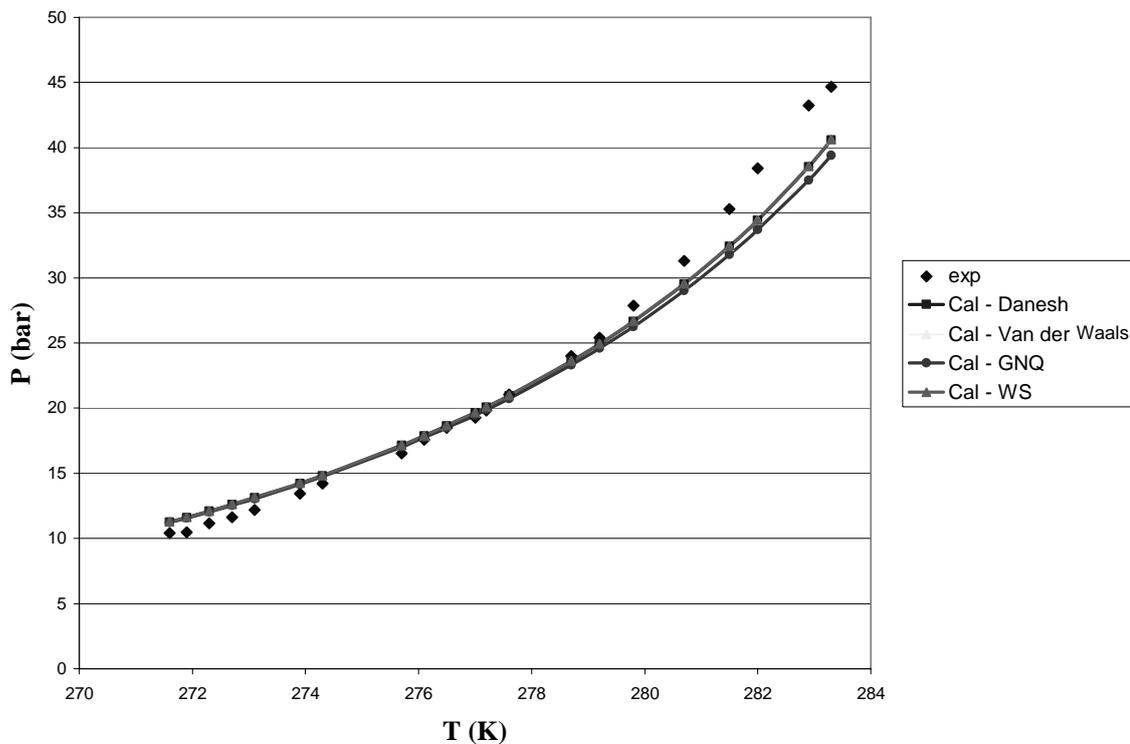


Figure 6. three phase equilibrium curve of carbon dioxide hydrate based on four mixing rules by using PR equation of state

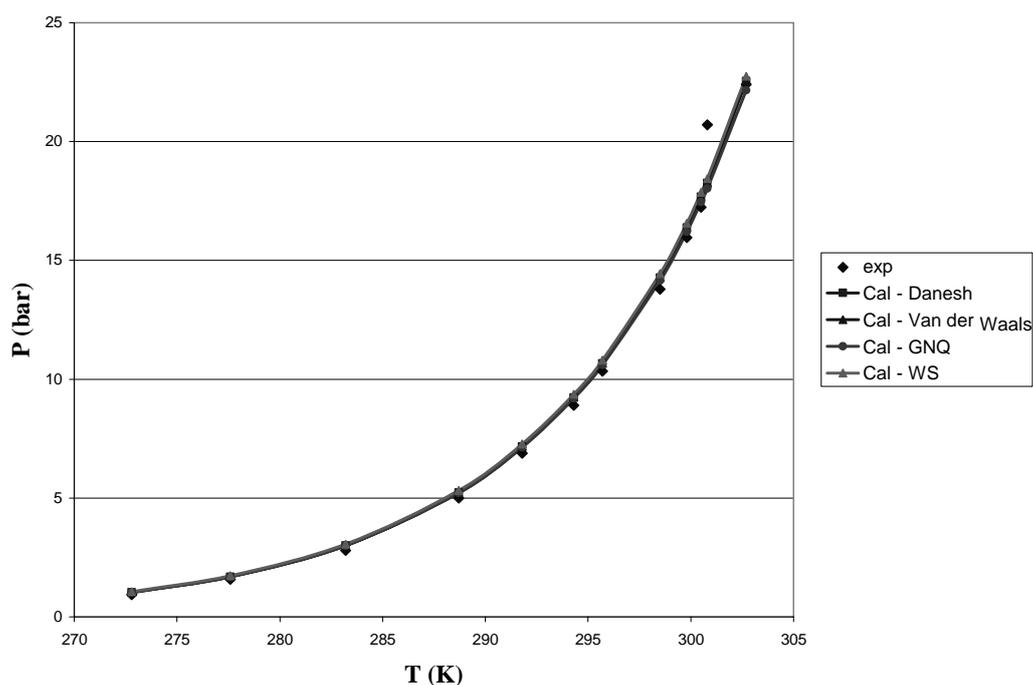


Figure 7. three phase equilibrium curve of hydrogen sulfide hydrate based on four mixing rules by using PR equation of state

A summary of results and error percentage for the predicted pressure is given in Table 6 at all studied systems. As shown in this table,

the GNQ mixing rule has the minimum error percent.

Table 6. Summary of three phase equilibrium calculation results (VL_wH), by using PR EOS and four mixing rules, in six binary mixtures in the considered rang of temperature and pressure

				$\overline{Error} = \frac{1}{NP} \sum_{i=1}^{NP} \frac{ P_i^{cal} - P_i^{exp} }{P_i^{exp}}, \%$			
Mixture	T range (K)	P range (bar)	No. of Points	Danesh MR	Van der Waals MR	GNQ MR	WS MR
CH ₄ -H ₂ O	262.4-320.1	17.9-3970	38	11.62	13.16	16.74	12.33
C ₂ H ₆ -H ₂ O	273.7-286.5	5.1-27.30	16	15.78	15.84	5.27	15.89
C ₃ H ₈ -H ₂ O	273.2-278.4	1.65-5.62	16	4.68	4.76	3.31	4.65
iC ₄ H ₁₀ -H ₂ O	273.2-275	1.10-1.65	17	1.77	1.76	0.71	3.19
CO ₂ -H ₂ O	271.6-283.3	10.40-44.68	34	5.50	5.51	5.84	5.57
H ₂ S-H ₂ O	272.8-302.7	0.93-22.41	19	5.20	5.21	4.92	6.71
				7.42%	7.70%	6.13%	8.05%

4- Conclusions

In all of the studied mixtures (except CH₄ hydrate and CO₂ hydrate), among the mixing rules (with VPT equation), GNQ mixing rule for predicting equilibrium pressure with an average percent of error 6%, is more suitable. It is considerable that the calculated pressure from the GNQ rule is highly dependent on optimized interaction parameters.

Obtained equilibrium pressure from Van der Waals mixing rule is closest to the results of the WS mixing rule. Although the WS mixing is based on Gibbs free energy and has more difficulty than other mixing rules, the results are not suggested, so using it is not recommended.

Calculated results for methane fraction in liquid phase shows that, the Danesh mixing rule for predicting concentrations of liquid is more suitable, because this rule considers the polarity components (H₂O molecule).

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