

Prediction of Structural Changes in Gas Hydrate for Methane and Ethane Mixture by Using Tangent Plane Distance Minimization

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Abstract: In this study, the change in the crystalline structure of gas hydrate was predicted for ternary mixture of methane-ethane-water. For this purpose, the tangent plane distance (TPD) minimization method was used. First, the calculations were performed for the binary mixtures of methane-water and ethane-water as the gas and liquid phases. The results show that for a binary mixture of these components in the gas phase, at the temperatures of 274 K and 275 K, for a wide range of pressure, the phase remains stable; however, the liquid phase is unstable and it splits into two or more new phases. The method was used for any possible new phases and the stable new phases determined by TPD minimization. By using this method for the ternary mixture at 20 different points (pressure and composition) at the temperature of 277.6 K, the results for stable phases are found to be consistent with the literature; further, a structural change from sI to sII is observed at methane mole fraction of 0.74, and another structural change from sII to sI is observed at methane mole fraction of 0.99 at 277.6 K. This method can be used for the stability analysis of more points to predict the boundary of the phase diagram and stable zone for different phases. In this study, the genetic algorithm was used for minimization of TPD function.

Keywords: Methane, Ethane, Structural changes, Stability, Gas hydrate

1. Introduction

Gas hydrates are ice-like crystalline structures formed with water in the presence of light gases such as methane (C_1) or ethane (C_2) under high pressure and at low temperature which is close to freezing point of water. These light gases are trapped in several different cages

that can form different crystalline structures such sI, sII or sH .

Since C_1 and C_2 are the two major components of natural gases, hydrates formed from these gases and their mixtures are significant. The equilibrium conditions of hydrate formation of these pure components and their binary mixtures are reported (Holder & Hand, 1982).

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Until the late 1990s, it was believed that the hydrate formed from a mixture of C_1 and C_2 would always be sI. However, it has recently been experimentally observed by Subramanian, Ballard and Sloan (2000) that the gas mixture of C_1 and C_2 can form sII hydrate at certain composition. For methane and ethane mixture, the structural change from sI to sII occurs over a methane vapor composition range (y_{CH_4}) of 0.72-0.75. In this study, structure II is formed at ($y_{CH_4} = 0.74$) and the composition of mixture at this point, while considering 95% of composition of mixture for water, is 0.037, 0.013, 0.95 for methane, ethane and water respectively. The other structural change from sII to sI occurs at ($y_{CH_4} = 0.99$) and composition of mixture at this point is 0.049, 0.001, 0.95.

Michelsen (1982) presented a method for stability analysis of gas hydrate at certain temperatures and pressures and this method is based on minimization of tangent plane distance (TPD) of Gibbs energy of system.

New Kihara potential parameters for C_1 and C_2 to predict the structural change from sI to sII were used by Ballard and Sloan (2000). Clarke and Bishnoi (2003) reported new Kihara potential parameters that can be used for thermodynamic modeling of structural changes in Van der Waals and Platteeuw model (Van der Waals & Platteeuw, 1959).

In this Study, the structural changes at different zones of the phase diagram were studied by using the minimization of the TPD function..

2. TPD Minimization

The vertical distance from the tangent hyper plane to the molar Gibbs energy surface of system at initial composition (\bar{z}) to the energy surface of system at another composition such as (\bar{x}) can be written as follows (Michelsen, 1982, p. 2):

$$TPD(\bar{x}) = \sum_{i=1}^{NC} x_i (\mu_i(\bar{x}) - \mu_i(\bar{z})) \quad (1)$$

where μ_i is the chemical potential of component i in the mixture and NC is the total number of components. Moreover, we have a constraint for Eq. (1):

$$\sum_{i=1}^{NC} x_i = 1 \quad , \quad 0 \leq x_i \leq 1 \quad (2)$$

By the minimization of TPD function by considering Eq. (2), the amount of minimized function, TPD^* , can be used for the stability analysis of the primary mixture at initial composition (\bar{z}). Subsequently, if $TPD^* \geq 0$, the system is stable and if $TPD^* < 0$, the system is unstable.

By differentiation of Eq. (1) with respect to the $NC - 1$ independent mole fraction, the following stationary condition can be found:

$$\mu_i(\bar{x}) - \mu_i(\bar{z}) = K \quad (3)$$

where K is independent of the component index i .

By using the equations of state for the calculation of fugacity, it is more convenient to work in terms of fugacity coefficients; thus, the stability criterion can be written as follows:

$$\ln x_i + \ln \phi_i(\bar{x}) - \ln z_i - \ln \phi_i(\bar{z}) = \frac{K}{RT} = k \quad (4)$$

$i = 1, 2, \dots, NC$

The new variable $X_i = x_i \exp(-k)$ can be interpreted in terms of mole numbers, and Eq. (4) can be written as follows (Michelsen, 1982, p. 5):

$$TPD(\bar{x}) = 1 + \sum_{i=1}^{NC} X_i (\ln X_i + \ln \phi_i(\bar{x}) - \ln z_i - \ln \phi_i(\bar{z}) - 1) \quad (5)$$

Where

$$x_i = \frac{X_i}{\sum_{i=1}^{NC} X_i} \quad (6)$$

By using X_i , the constraint (i.e., Eq. (2)) is simplified as:

$$X_i \geq 0 \quad (7)$$

Therefore, TPD function only with the restriction of $X_i \geq 0$ can be minimized in order to obtain TPD^* by any optimization method like genetic algorithm.

When the system is unstable, the concentrations that minimize the TPD function (\bar{x}^*) are a good initial guess for the composition of components in the new phase. When the system is unstable, by using these concentrations for the composition of components in the new phase, we can calculate and minimize the TPD function for any new phase. Then according to stability criterion, we can determine the number and type of phases that exist in equilibrium; subsequently, the amount and composition of new phases can be calculated by flash calculation.

3. Fugacity Calculation of Different Phases

In this study, the fugacity of the components in vapor and liquid phases was calculated by using equation of state of Valderrama- Patel and Teja (Valderrama, 1990).

Equations of state in general form are shown through the following relation:

$$P = \frac{RT}{v-b} - \frac{a}{v^2+Uv+W} \quad (8)$$

a and b parameters are calculated by the next two following equations:

$$\left(\frac{\partial P}{\partial v}\right)_{\text{critical}} = 0 \quad (9)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{\text{critical}} = 0 \quad (10)$$

Coefficients of Valderrama- Patel and Teja equation of state based on general form of equation of state are shown in Table 1.

Table 1. Coefficients of Valderrama- Patel and Teja equation of state

Equation	Valderrama-Patel&Teja
U	b+c
W	-bc
Ω_a	0.66121-0.79105 Z_c
Ω_b	0.02207+0.20868 Z_c
Ω_c	0.57765-1.8708 Z_c
$\alpha(T_r)$	$(1+m(1-\sqrt{T_r}))^2$
m	0.46283+3.5823(ωZ_c)+8.1941 $Z_c(\omega Z_c)^2$

a, b and c parameters are defined by using the following relations:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \alpha(T_r) \quad (11)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (12)$$

$$c = \Omega_c \frac{RT_c}{P_c} \quad (13)$$

In this study, binary interaction parameters reported in Heriot Watt Hydrate software, HWHYD (ver. 1.1), for methane-ethane system and based on Valderrama-Patel and Teja equation of state were used (Valderrama, 1990).

The fugacity of the water and hydrate formers in solid phase (sI or sII) can be calculated by using Van der Waals and Platteeuw model (Van der Waals & Platteeuw, 1959) and the Kihara potential parameters reported by Avlonitis, Danesh, and Todd (1994) for the calculation of Langmuir constant.

4. Calculation Procedure

By determining the temperature and pressure and feed composition of the mixture, the fugacity of components in the mixture was calculated. Then, by using genetic algorithm

the TPD function was minimized. When the TPD* value was positive, the mixture at that pressure and temperature and feed composition was stable, and when the TPD* value was negative, the mixture at that pressure and temperature and feed composition was not stable and could be split into new phases. In this case, for determining of these new phases, the calculation procedure was repeated.

5. Results

The genetic algorithm was used for the minimization of TPD function due to the complexity of multivariable function. Genetic algorithm, one of the optimization methods, is based on ecological patterns and acts at random. This method is very useful in optimizing multivariable functions or functions with complex derivatives. Genetic algorithm consists of steps such as generating the initial population, encoding variables, assessing variables with target function, selecting the best variables, exchanging information, mutating information, and finally repeating these steps to reach the best answers.

In this study, stability analysis calculations for methane-water system and ethane-water system were performed at two steps. In the first step, TPD function for vapor and liquid phases was calculated and minimized. The results of calculation show that for all temperatures and pressures if the system with composition \bar{z} is in the form of gas phase, the methane-water and ethane-water mixtures are stable, but if the initial system with composition \bar{z} is taken as the liquid phase, it becomes unstable by increasing the pressure at specified temperature.

The pressure at which the sign of TPD* changes is the equilibrium pressure of hydrate formation at the given temperature.

In the second step, the concentrations that minimize the TPD function (\bar{x}^*) were used as the composition of components in the new phase, and for determining the number and type of stable phases in equilibrium state, TPD function for any phase was calculated and minimized again.

The accuracy of TPD model in this study with experimental data for methane-water system and for the prediction of equilibrium pressure of hydrate formation was evaluated. The results of comparison with experimental data show that TPD model has a very good accuracy, and average of error for methane-water system is 3.51%.

5.1. Methane-water system at 274 K and 275 K and composition (0.5, 0.5)

The results for methane-water vapor and liquid phases are shown in Figs. 1 and 2 (at 274 K) and Figs. 3 and 4 (at 275 K)

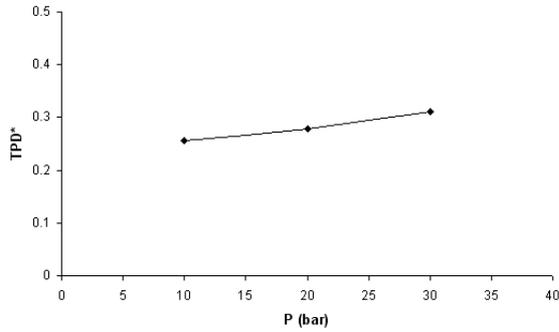


Figure 1. TPD* versus Pressure for vapor phase of methane-water system at 274 K

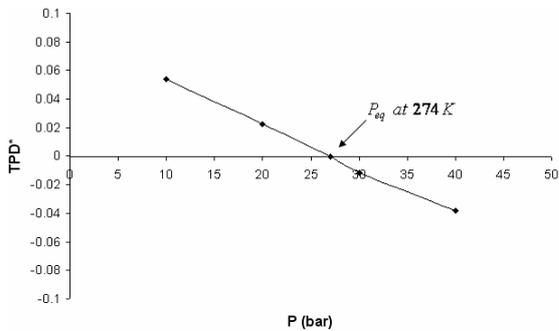


Figure 2. TPD* versus Pressure for liquid phase of methane-water system at 274 K

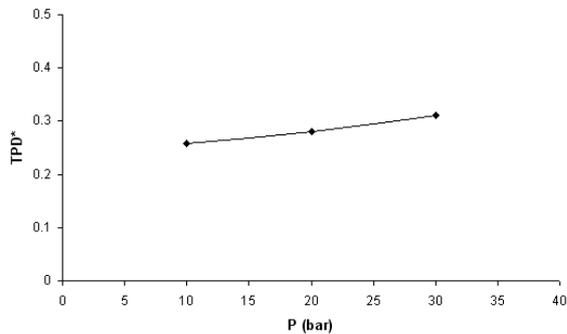


Figure 3. TPD* versus Pressure for vapor phase of methane-water system at 275 K

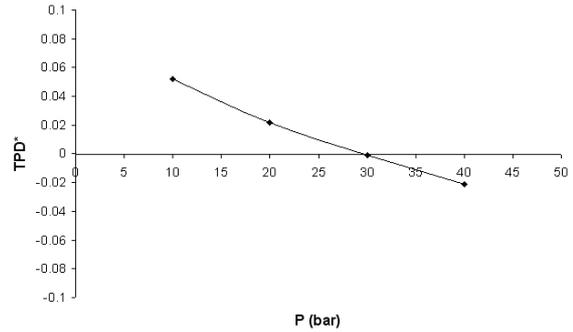


Figure 4. TPD* versus Pressure for liquid phase of methane-water system at 275 K

According to vapor phase diagram (Figs. 1 and 3), the sign of TPD* is positive and therefore the vapor phase is stable; and according to liquid phase diagram (Figs. 2 and 4), the sign of TPD* is found to change at certain pressures (27 and 30 bars). Therefore, above these pressures and at higher pressures, the liquid phase is unstable.

In this step, for determining the number and type of phases that can be produced due to the splitting of liquid phase, the TPD function for any new phase is determined again and the minimization process is repeated. For checking the validation of the results, the equilibrium pressures for C₁ at 274 K and 275 K were compared with the results of Heriot Watt Hydrate software, HWHYD (ver. 1.1), as shown in Table 2; and also the results of TPD minimization calculation for methane-water mixture at 274 K and 275 K are shown in Tables 3 and 4.

On the basis of the results of Tables 3 and 4, and the stability criterion (TPD* ≥ 0), it can be concluded that the splitting of the unstable liquid phase leads to the formation of two stable phases (new liquid & sl).

Table 2. Equilibrium pressure of hydrate formation derived by TPD minimization method with the results of HWHYD

T(K)	P _{eq} ^{This Work}	P _{eq} ^{HWHYD}	% Error
274	27	29.4	8.1
275	30	32.4	7.4

Table 3. TPD* for liquid phase of methane(1)-water(2) system at 274 K

T= 274 K	Z ₁	Z ₂	TPD*			
			New Liquid	Vapor	Hydrate I	Hydrate II
P=27 bar	0.00315	0.99685	0.01415	-0.03242	0.01439	-0.01105
P=30 bar	0.00520	0.99480	0.02632	-0.03988	0.02214	-0.01544
P=40 bar	0.00593	0.99407	0.06173	-0.04164	0.02527	-0.02213

Table 4. TPD* for liquid phase of methane(1)-water(2) system at 275 K

T= 275 K	Z ₁	Z ₂	TPD*			
			New Liquid	Vapor	Hydrate I	Hydrate II
P= 30 bar	0.00414	0.99586	0.02997	-0.02296	0.01354	-0.01326
P= 40 bar	0.00485	0.99515	0.03435	-0.03621	0.02497	-0.01342

5.2. Ethane-water system at 274 K and 275 K and composition (0.5, 0.5)

The results for ethane-water vapor and liquid phases are shown in Figs. 5 and 6 (at 274 K) and Figs. 7 and 8 (at 275 K)

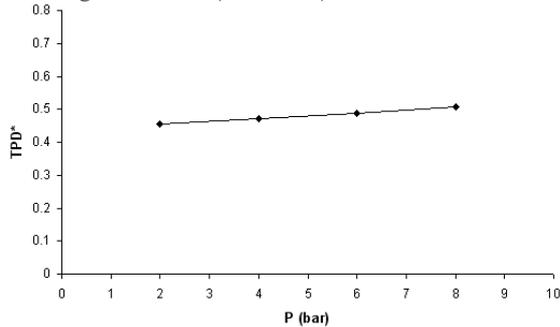


Figure 5. TPD* versus Pressure for vapor phase of ethane-water system at 274 K

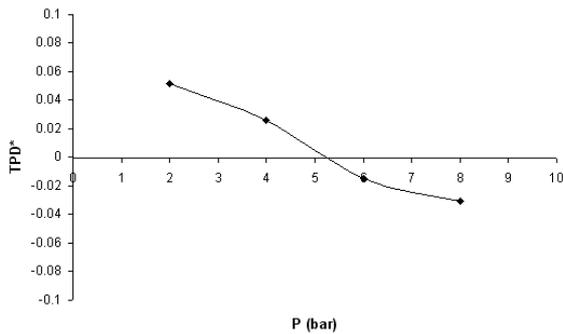


Figure 6. TPD* versus Pressure for liquid phase of ethane-water system at 274 K

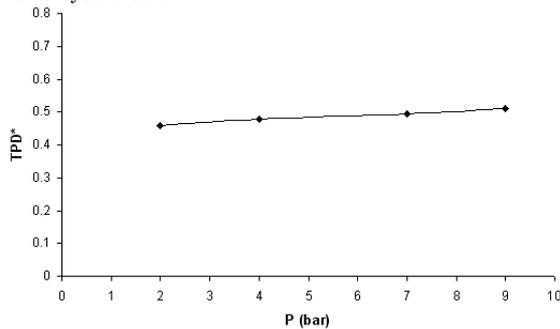


Figure 7. TPD* versus Pressure for vapor phase of ethane-water system at 275 K

Table 6. TPD* for liquid phase of ethane(1)-water(2) system at 274 K

T= 275 K	Z ₁	Z ₂	TPD*			
			New Liquid	Vapor	Hydrate I	Hydrate II
P= 6 bar	0.00052	0.99948	0.16854	-0.02186	0.01677	-0.01636
P= 8 bar	0.00076	0.99924	0.25690	-0.05773	0.02720	-0.02689

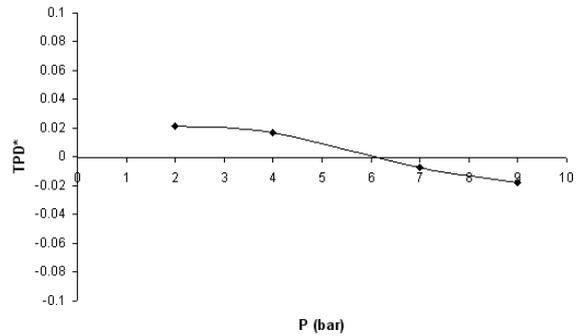


Figure 8. TPD* versus Pressure for liquid phase of ethane-water system at 275 K

The vapor phase diagram at 274 K and 275 K and at different pressures is stable (Figs. 5 and 7). The change of sign of TPD* for liquid phase diagram, at certain pressure (Figs. 6 and 8) causes the splitting of liquid phase.

By repeating the TPD minimization for any new possible phases, the number and type of phases can be determined.

The validation of the calculated equilibrium pressure for C₂ at 274 K and 275 K is done by comparing them with the results of Heriot Watt Hydrate software, HWHYD (ver. 1.1), as shown in Table 5. The results of TPD minimization for this mixture at 274 K and 275 K are shown in Tables 6 and 7.

According to the results, it can be concluded that the splitting of the unstable liquid phase leads to the formation of two stable phases (new liquid & sl).

Table 5. Equilibrium pressure of hydrate formation derived by TPD minimization method with the results HWHYD

T (K)	p _{eq} ^{This Work}	p _{eq} ^{HWHYD}	% Error
274	5.2	5.1	1.9
275	6.1	5.8	5.1

Table 7. TPD* for liquid phase of ethane(1)-water(2) system at 275 K

T= 275 K	Z ₁	Z ₂	TPD*			
			New Liquid	Vapor	Hydrate I	Hydrate II
P= 7 bar	0.00073	0.99927	0.17901	-0.01242	0.01468	-0.01522
P= 9 bar	0.00085	0.99915	0.30578	-0.02171	0.02719	-0.02591

5.3. Structural Changes of Gas Hydrate in Methane-Ethane-Water Mixture

In the previous section, it was shown that pure methane and pure ethane form only sI hydrate. In contrast to the general prediction that sI hydrate will be formed for methane and ethane mixture, the experimental data shows these mixtures show different behaviors at different compositions. Methane and ethane gas mixtures at certain compositions show structural changes in hydrate formation.

Fig. 9 shows the complete pressure versus composition phase diagram for the methane and ethane mixture at 277.6 K reported by Subramanian et al. (2000). This diagram was obtained by using Gibbs energy minimization method. Hydrate equilibrium data under L_w – H – V equilibrium conditions by Deaton and Frost Jr, (1946) are also plotted to compare the model predictions with experimental data. According to Fig. 9, the incipient hydrate structure changes from sI to sII is predicted at y_{CH₄} = 0.74, and with increasing methane

concentration, the upper transition point from sII to sI is predicted to occur at approximately 99.3 mol % methane.

The noticeable point in this diagram is the coexistence of sI and sII for initial compositions of approximately 0.4-0.6 methane when the pressure is increased to approximately 1.7 MPa and above. A similar region is predicted in the composition range of approximately 0.9-0.95 methane when the pressure is above 4 MPa.

In this research, for the study of structural changes in methane and ethane mixture according to the TPD method, 20 points were considered in various regions of this diagram (Fig. 9). Subsequently, the TPD function at 277.6 K, for various pressures and compositions for any phase was calculated and minimized. The results are shown in Tables 8 to 13 and are in good agreement with the diagram presented.

For example, according to the results of Table 9 at point 6, only L_w, sI and sII phases coexist.

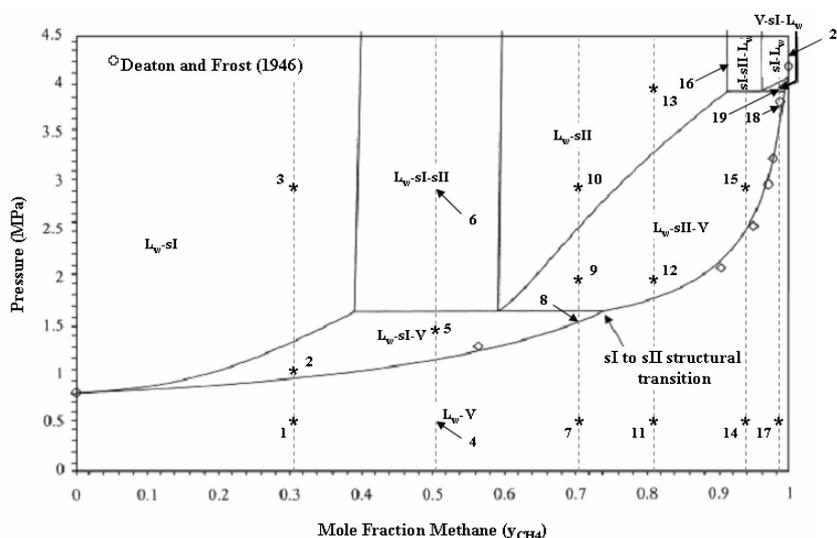


Figure 9. The complete pressure versus composition phase diagram for methane+ethane+water system at 277.6 K (Subramanian, Kini, Dec, & Sloan Jr, 2000)

Table 8. TPD* for methane+ethane+water system at 277.6 K and component composition (0.015, 0.035, 0.95)

T= 277.6 K	Point	L _w	V	S I	S II
P= 0.5 MPa	1	0.18476	0.10951	-0.42806	-0.21015
P= 1.0 MPa	2	0.17749	0.30982	0.39139	-0.26387
P= 3.0 MPa	3	0.19034	-0.01791	0.36583	-0.37286

Table 9. TPD* for methane+ethane+water system at 277.6 K and component composition (0.025, 0.025, 0.95)

T= 277.6 K	Point	L _w	V	S I	S II
P= 0.5 MPa	4	0.17367	0.12554	-0.38029	-0.19347
P= 1.5 MPa	5	0.17606	0.42515	0.22196	-0.27664
P= 3.0 MPa	6	0.22048	-0.03014	0.36888	0.43189

Table 10. TPD* for methane+ethane+water system at 277.6 K and component composition (0.035, 0.015, 0.95)

T= 277.6 K	Point	L _w	V	S I	S II
P= 0.5 MPa	7	0.19026	0.15861	-0.31511	-0.17974
P= 1.6 MPa	8	0.18711	0.44583	0.40156	-0.28073
P= 2.0 MPa	9	0.19581	0.49762	-0.57129	0.25824
P= 3.0 MPa	10	0.21571	-0.03701	-0.64132	0.25043

Table 11. TPD* for methane+ethane+water system at 277.6 K and component composition (0.04, 0.01, 0.95)

T= 277.6 K	Point	L _w	V	S I	S II
P= 0.5 MPa	11	0.17569	0.14661	-0.26903	-0.16775
P= 2.0 MPa	12	0.17961	0.51473	-0.35729	0.25164
P= 4.0 MPa	13	0.21037	-0.01041	-0.65259	0.23169

Table 12. TPD* for methane+ethane+water system at 277.6 K and component composition (0.047, 0.003, 0.95)

T= 277.6 K	Point	L _w	V	S I	S II
P= 0.5 MPa	14	0.19658	0.24325	-0.17451	-0.10582
P= 3.0 MPa	15	0.20443	0.60223	-0.47262	0.27611
P= 4.3 MPa	16	0.21348	-0.01865	0.40776	0.24997

Table 13. TPD* for methane+ethane+water system at 277.6 K and component composition (0.049, 0.001, 0.95)

T= 277.6 K	Point	L _w	V	S I	S II
P= 0.5 MPa	17	0.18244	0.27738	-0.13489	-0.06519
P= 3.9 MPa	18	0.20354	0.63812	-0.47603	0.26354
P= 4.05MPa	19	0.19424	0.64246	0.39974	-0.30255
P= 4.3 MPa	20	0.19966	-0.02326	0.41808	-0.31525

6. Conclusion

For any flash calculations, it is important to know the number and type of phases that are in equilibrium. Therefore, stability analysis calculations must be performed before flash calculations. In this study, the TPD minimization method was used to determine the number and type of phases in equilibrium for pure methane and pure ethane. Subsequently, by using TPD method, the structural changes of the gas hydrate for methane and ethane mixture have also been discussed. The TPD method helps in determining structural changes of gas hydrate in methane and ethane mixture and by using this method, the phase boundary can be determined by repeating the calculations for different points.

Acknowledgments

Funding for this work was provided by the gas company of Semnan province.

Nomenclature

K	chemical potential difference
k	dimensionless chemical potential difference
NC	number of component
P	pressure
P _c	critical pressure
R	ideal gas constant
T	temperature
T _c	critical temperature
T _r	reduced temperature
v	molar volume

x_i	mole fraction of component i
\bar{x}^*	concentration that minimize TPD function
X_i	mole number of component i
Z	component composition of mixture
Z_c	critical compressibility factor
TPD	tangent plane distance, objective function
TPD*	minimum of TPD function
ϕ_i	fugacity coefficient of component i
μ_i	chemical potential of component i
α	temperature function in VPT EOS
ω	acentric factor
$\Omega_a, \Omega_b, \Omega_c$	parameters in VPT EOS

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