



## Determination of Structure and Formation Conditions of Gas Hydrate by Using TPD Method and Flash Calculations

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### Abstract

In this work, stability calculations and determination of gas hydrate structure in equilibrium conditions by using minimization of TPD function for methane-water system (SI), propane-water system (SII) and methane-methyl cyclo pentane-water system (SH) were performed. Based on results, at 274 K and 275 K temperatures, the liquid phase of methane-water system at 27 bar and 30 bar pressures, propane-water system at 1.7 bar and 2.5 bar pressures and methane-methyl cyclo pentane-water system at 9.6 bar and 10.1 bar pressures was decomposed. As a result of decomposition of liquid phase for these systems, two new phases, a new liquid phase and hydrate phase were formed. Subsequently, multiphase flash calculations in order to determine the amount and composition of stable phases in equilibrium state were performed. For minimization of TPD function, Algorithm Genetic was used. The results Show good accuracy with data of Heriot Watt university hydrate model (HWHYD).

**Keywords:** Tangent plane distance, Multiphase flash calculation, Gibbs energy minimization, Gas Hydrate.

### Research Highlights

- Determination of thermodynamic conditions of gas hydrate formation by using minimization of tangent plane distance from Gibbs energy surface (TPD method).
- Determination of numbers and type of stable phases in equilibrium state in order to performing multiphase flash calculations.
- Calculation of amount and composition of stable phases in equilibrium state.

## 1. Introduction

Gas hydrates are ice-like crystalline structures that forms in the presence of light gases such as methane and ethane or non-hydrocarbons gases such as nitrogen and carbon dioxide with water. These gases are trapped in several different cages that forms different crystalline structures like sI, sII or sH. Stability of gas hydrate crystalline is the result of hydrogen bonds between water molecules and van der waals forces between water and gas molecules in structure lattice of hydrate.

After designing the first gas transfer pipeline, blockage of pipelines with gas hydrate by Hammerschmidt [1] in United State was introduced. Subsequent to this phenomenon, methods of prevention of gas hydrate formation in pipelines were studied.

For the first time, thermodynamic principles of gas hydrate by Van der waals and Platteeuw [2] were studied. Because of the problems that were the result of gas hydrate formation, many studies about prediction of gas hydrate formation conditions and stability of gas hydrate were performed. Michelsen [3] proposed a method for stability analysis calculations at certain temperature and pressure. This method is based on minimization of tangent plane distance from Gibbs energy surface (TPD method).

## 2. TPD Method

The distance between tangent hyperplane to Gibbs energy of system at initial composition ( $\bar{z}$ ) and system at another composition like ( $\bar{x}$ ) can be written as follow:

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

where,  $\mu_i$  is the chemical potential of component i in the mixture and NC is the total number of components. Also we have a constraint for Eq. 1 as:

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

When the TPD function for variables  $x_i (i = 1, \dots, NC)$  with considering Eq. 2 to be minimized; the amount of minimized function ( $TPD^*$ ) is the stability analysis of the primary mixture at composition  $\bar{x}$ . Subsequently if  $TPD^* \geq 0$ , the system is stable and if  $TPD^* < 0$ , the system is unstable.

Since all minima of  $TPD(\bar{x})$  are located in the interior of the permissible region in Eq. (2),  $TPD(\bar{x})$  will be non-negative, if it is non-negative at all stationary point, that is, points where the derivatives with respect to all independent variables equal zero.

By differentiation of Eq. 1 respect to the  $NC-1$  independent mole fractions yield the stationary condition [3]

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

Where K is independent of the component index i.

For equations of state calculations, it is more convenient to work in terms of fugacity coefficients, thus stability criterion can be written as:

$$\ln x_i + \ln \phi_i(\bar{x}) - \ln z_i - \ln \phi_i(\bar{z}) = \frac{K}{RT} = k \quad i = 1, 2, \dots, NC \quad (4)$$

With the new variables  $x_i = x_i \exp(-k)$ , that the new independent variables  $x_i$  can formally be interpreted as mole numbers, the Eq. 4 can be written as follow [3]



$$TPD(\bar{x}) = 1 + \sum_i X_i (1 - n_i X_i + 1 - n_i \phi_i(\bar{x}) - 1 - n_i z_i - 1 - n_i \phi_i(\bar{z}) - 1) \geq 0 \quad (5)$$

where;

$$x_i = \frac{X_i}{\sum_i X_i} \quad (6)$$

By using  $x_i$ , the constraint (Eq. 2) is converted to a more simple constraint.

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

Therefore, we can minimize TPD function with only restriction of  $x_i \geq 0$  to obtain TPD\*.

When the system is unstable, concentrations that minimize this function ( $\bar{x}^*$ ), are good initial guesses for components composition in the new phase.

When the system is unstable, by using these concentrations for components composition in the new phase, we can calculate and minimize TPD function for any phase. Then according to stability criterion, the numbers and type of phases in equilibrium state are determined and subsequently the amount and composition of new phases can be calculated by flash calculations.

### 3. Calculation of fugacity of components in vapor and liquid phases

In this work, the fugacity of components in vapor and liquid phases is calculated by using Valderama-Patel & Teja equation of state [4,5].

### 4. Calculation of fugacity of components in solid phase (SI, SII)

The fugacity of components in solid phase (SI, SII) by using Van der Waals and Platteeuw model [2] and the Kihara potential parameters that are reported by Avlonitis et al. [5] is calculated.

### 5. Calculation of fugacity of components in solid phase (SH)

The fugacity of components in solid phase (SH) is calculated as following method [6]:

In structure H of gas hydrate according to numbers of cavities writing would be possible;

$$\alpha_k = \frac{C_{k1}}{C_{k2}} \quad (8)$$

$$\beta_k = \frac{C_{k2}}{C_{k3}} \quad (9)$$

In these equations,  $C_{kj}$ , are langmuir coefficients of cavities. With definition of  $\theta_1$  and  $\theta_2$  as follow:

$$\theta_1 = \frac{v_2 n_{02}}{N_0} \quad (10)$$

$$\theta_2 = \frac{v_3 n_{03}}{N_0} \quad (11)$$

that, in above equations  $n_{0j}$  is a fraction of  $j$  cavities that are empty and  $N_0$  is the number of empty cavities for any mole of water. Subsequently;

$$F(\theta_1, \theta_2) = \sum_{k=1}^{NC-1} N_k \frac{\theta_1 \beta_k}{\alpha_k \beta_k [1 - (\theta_1 + \theta_2)] + \theta_1 \beta_k + \theta_2 \alpha_k} + \theta_1 N_0 - v_2 = 0 \quad (12)$$

$$G(\theta_1, \theta_2) = \sum_{k=1}^{NC-1} N_k \frac{\theta_2 \alpha_k}{\alpha_k \beta_k [1 - (\theta_1 + \theta_2)] + \theta_1 \beta_k + \theta_2 \alpha_k} + \theta_2 N_0 - v_3 = 0 \quad (13)$$

By solving these two nonlinear equations by using Newton-Raphson method,  $\theta_1$  and  $\theta_2$  are calculated. With determination of  $\theta_1$  and  $\theta_2$ , fugacity of components in solid phase (SH) is calculated by Eq 14.

$$f_k = \frac{N_k \beta_k}{N_0 C_{k2} \alpha_k \beta_k [1 - (\theta_1 + \theta_2)] + \theta_1 \beta_k + \theta_2 \alpha_k} \quad (14)$$

The fugacity of water in hydrate phase (SH) is calculated by Eq 15.

$$\ln f_w^H - \ln f_w^M = v_1 \ln \left( \frac{[1 - (\theta_1 + \theta_2) N_0]}{v_1} \right) + v_2 \ln \left( \frac{\theta_1 N_0}{v_2} \right) + v_3 \ln \left( \frac{\theta_2 N_0}{v_3} \right) \quad (15)$$

in above equation,  $f_w^M$  is the fugacity of water in empty lattice of hydrate.

## 6. Flash calculations

In flash calculations, first at distinct pressure and temperature and with primary guess of mole fraction of components in liquid and vapor phase and by using Valderama- Patel & Teja equation of state, the fugacity of components in liquid and vapor phases is calculated. Subsequently, by using the fugacity of components in vapor phase and with considering equality of fugacity of one component at equilibrium state in all phases, mole fraction of components in hydrate phase is calculated. With determination of mole fractions in hydrate phase, by using Teta method [7], fugacity of components in hydrate phase is calculated.

With determination of mole fractions, the distribution coefficient of component  $i$  in phase  $j$  and with selection of one phase as reference phase (with index 1 for reference phase) is calculated by using the following equation.

$$K_{ij} = \frac{\phi_{ij}}{\phi_{i1}} = \frac{x_{i1}}{x_{ij}} \quad i = 1, \dots, NC \quad (16)$$

$$j = 1, \dots, NP$$

According to this point that in calculations of gas hydrate formation, the vapor phase is always present, we can consider this phase as reference phase. By writing mass balance equations, we can obtain the below relations;

$$Z_i = x_{i1} \left( 1 + \sum_{j=2}^{NP} F_j \left( \frac{1}{K_{ij}} - 1 \right) \right) \quad (17)$$

$$x_{i1} = \frac{Z_i}{1 + \sum_{j=2}^{NP} F_j \left( \frac{1}{K_{ij}} - 1 \right)} \quad i = 1, \dots, NC \quad (18)$$



$$x_{i,m} = \frac{\frac{Z_i}{K_{i,m}}}{1 + \sum_{j=2}^{NP} F_j \left( \frac{1}{K_{i,j}} - 1 \right)} \quad i = 1, \dots, NC \quad (19)$$

$$j = 2, \dots, NP$$

subsequently;

$$\sum_{i=1}^{NC} (x_{i,m} - x_{i1}) = 0 \quad m = 2, \dots, NP \quad (20)$$

$$\sum_{i=1}^{NC} \frac{\left( \frac{1}{K_{i,m}} - 1 \right) Z_i}{1 + \sum_{j=2}^{NP} F_j \left( \frac{1}{K_{i,j}} - 1 \right)} = 0 \quad m = 2, \dots, NP \quad (21)$$

These two nonlinear equations with primary guesses for  $K_{ij}$  and  $F_j$  and by using Newton-Raphson method are solved. With determination of new amount of  $F_j$  and calculation of  $x_{ij}$  through using relations, equality of fugacities by using Eq 22. can be checked.

$$\sum_{i=1}^{NC} \sum_{j=1}^{NP} \left( \ln \frac{f_{i,j}}{f_{i1}} \right)^2 < 10^{-6} \quad (22)$$

If equality of fugacities is not established, new amounts of  $K_{ij}$  are calculated by the below equation.

$$K_{i,j}^{t+1} = K_{i,j}^t \left( \frac{f_{i,j}}{f_{i1}} \right)^t \quad i = 1, \dots, NC \quad (23)$$

$$j = 2, \dots, NP$$

that, index t represents computation times.

## 7. Results and discussion

One of the important calculations before equilibrium calculations is determination of numbers and type of phases in equilibrium state. In other words, without information about stable phases in equilibrium state, performing equilibrium calculations are impossible. In this work TPD method for stability analysis and determination of equilibrium pressure of gas hydrate formation for methane-water, propane-water and methane-methyl cyclo pentane-water systems are used. Calculations at 274 K and 275 K temperatures and various pressures are performed. Results of minimization of TPD function show that the vapor phase in any temperature and pressure is always stable, but the liquid phase in certain temperature and specific pressure is unstable and decomposed. As a result of decomposition of liquid phase two new phases are formed. When the system is unstable, concentrations that are minimize TPD function ( $\bar{x}^*$ ), are good initial guesses for components composition in the new phase. Subsequently, by using these concentrations for components composition in the new phase, again calculation and minimization of TPD function for any phase is performed. Then according to stability criterion, numbers and type of phases in equilibrium state are determined. Subsequently, multiphase flash calculations for determination of amount and

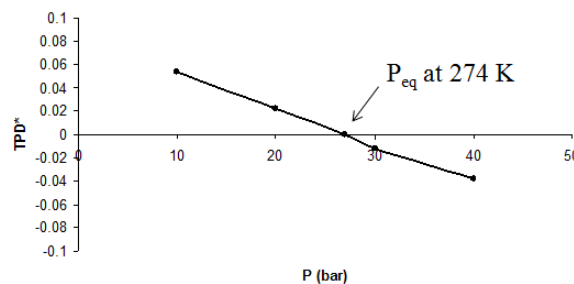
composition of phases in equilibrium state are performed. Algorithm Genetic is used for minimization of TPD function.

**7.1. methane-water system at 274 K and composition (0.5,0.5)**

The results of TPD function minimization for methane-water system show that the vapor phase is always stable, but liquid phase at certain temperature and specific pressure is unstable and decomposed. The results of minimization of TPD function for liquid phase of methane-water system are displayed in Table 1. According to this Table, TPD\* function for liquid phase of methane-water system at 27 bar pressure is negative and after this pressure, liquid phase is unstable and decomposed. Changes of TPD\* function versus pressure are displayed in Fig 1.

**Table 1. The results of calculation of TPD\* function for liquid phase of methane-water system at 274 K**

T = 274 K	TPD*	X* <sub>11</sub>	X* <sub>21</sub>
P = 10 bar	0.05389	0.00128	0.99872
P = 20 bar	0.02247	0.00304	0.99696
P = 27 bar	- 0.00002	0.00315	0.99685
P = 30 bar	- 0.01189	0.00520	0.99480
P = 40 bar	- 0.03806	0.00593	0.99407



**Fig 1. Changes of TPD\* function versus pressure for liquid phase of methane-water system at 274 K**

Concentrations that are minimize TPD function ( $\bar{x}^*$ ), are good initial guesses for components composition in the new phase. In order to determine the numbers and type of stable phases as a result of decomposition of unstable liquid phase, in this step TPD function for any phase in certain temperature and determined pressure and by using concentrations of first step as components composition in new phase is minimized. The results of this minimization are displayed in Table 2.

**Table 2. The results of calculation of TPD\* function for liquid phase of methane-water system by using concentrations as a result of first step minimization as components composition in the new phase at 274 K**



T = 274 K	Z <sub>1</sub>	Z <sub>2</sub>	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

Based on the results that displayed in Table 2. and with considering stability criterion ( $TPD^* \geq 0$ ), as a result of decomposition of unstable liquid phase, two stable phases, a new liquid and hydrate with structure I are formed. Subsequently, for determination of amount and composition of phases in equilibrium state, flash calculations are performed. The results of these calculations are shown in Table 3. and Fig 2.

Table 3. Composition and phases fraction in equilibrium state for methane-water system at 274 K

T = 274 K	P (bar)	Composition			Phase fraction		
		V	L <sub>w</sub>	H(I)	V	L <sub>w</sub>	H(I)
Methane	10	0.999367	0.000397	0.0	0.50012	0.49988	0.0
Water		0.000633	0.999603	0.0			
Methane	20	0.999694	0.000826	0.0	0.49974	0.50026	0.0
Water		0.000306	0.999174	0.0			
Methane	30	0.999803	0.001293	0.143166	0.49586	0.47889	0.02525
Water		0.000197	0.998707	0.856834			
Methane	40	0.999858	0.001802	0.144565	0.44205	0.15863	0.39932
Water		0.000142	0.998198	0.855435			

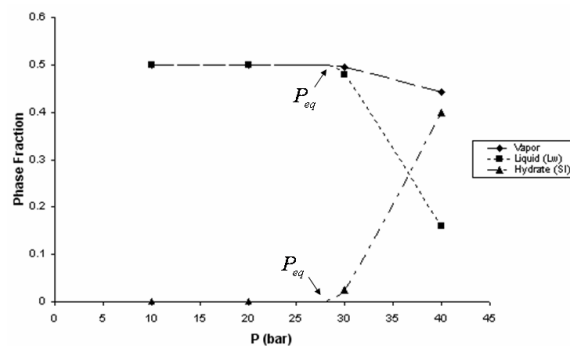


Fig 2. Changes of phase fraction versus pressure for methane-water system at 274 K

These calculations for methane-water system at 275 K temperature were performed and the results are shown below:

7.2. methane-water system at 275 K and composition (0.5,0.5)

Table 4. The results of calculation of TPD\* function for liquid phase of methane-water system at 275 K

T = 275 K	TPD*	X* <sub>11</sub>	X* <sub>21</sub>
P = 10 bar	0.05203	0.00235	0.99765
P = 20 bar	0.02184	0.00312	0.99688
P = 30 bar	- 0.00085	0.00414	0.99586
P = 40 bar	- 0.02121	0.00485	0.99515

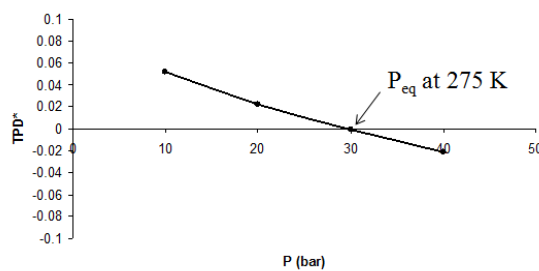


Fig 3. Changes of TPD\* function versus pressure for liquid phase of methane-water system at 275 K

Table 5. The results of calculation of TPD\* function for liquid phase of methane-water system by using concentrations as a result of first step minimization as components composition in the new phase at 275 K

T = 275 K	Z <sub>1</sub>	Z <sub>2</sub>	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

Table 6. Composition and phases fraction in equilibrium state for methane-water system at 275 K

T = 275 K	P (bar)	Composition			Phase fraction		
		V	L <sub>w</sub>	H(I)	V	L <sub>w</sub>	H(I)
Methane	10	0.999319	0.000389	0.0	0.50014	0.49986	0.0
Water		0.000681	0.999611	0.0			
Methane	20	0.999671	0.000809	0.0	0.49976	0.50024	0.0
Water		0.000329	0.999191	0.0			
Methane	30	0.999789	0.001265	0.142969	0.49816	0.49261	0.00923
Water		0.000211	0.998735	0.857031			
Methane	40	0.999847	0.001762	0.144419	0.44501	0.17588	0.37911
Water		0.000153	0.998238	0.855581			



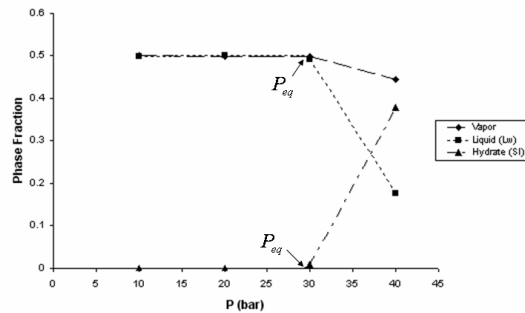


Fig 4. Changes of phase fraction versus pressure for methane-water system at 275 K

In this work equilibrium pressure of gas hydrate formation with experimental data and Heriot Watt university hydrate model (HWHYD) [8] is compared and the results show a good accuracy. Average error based on experimental data is 3.51% and the results of comparison with HWHYD model are displayed in Table 7.

Table 7. Comparison of equilibrium pressure of gas hydrate formation in methane-water system between TPD method and HWHYD model

T (K)	$P_{eq}^{TPD}$	$P_{eq}^{HWHYD}$	%Error
274	27	29.4	8.1
275	30	32.4	7.4

### 7.3. propane-water system at 274 k and composition (0.5,0.5)

The results of minimization of TPD function for liquid phase of propane-water system are shown in Fig 5.

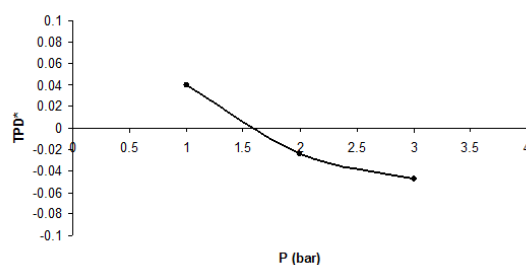


Fig 5. Changes of TPD\* function versus pressure for liquid phase of propane-water system at 274 K

As a result of decomposition of liquid phase of propane-water system, a new liquid and hydrate with structure II are formed. These results are shown in Table 8. The results of flash calculations for propane-water system are displayed in Table 9. and Fig 6.

Table 8. The results of calculation of TPD\* function for liquid phase of propane-water system by using concentrations as a result of first step minimization as components composition in the new phase at 274 K

T = 274 K	Z <sub>1</sub>	Z <sub>2</sub>	TPD*			
			New liquid	Vapor	Hydrate I	Hydrate II
P = 2 bar	0.00065	0.99935	0.25029	- 0.01836	- 0.00979	0.02345
P = 3 bar	0.00089	0.99911	0.31494	- 0.03126	- 0.01133	0.04674

Table 9. Composition and phases fraction in equilibrium conditions for propane-water system at 274 K

T = 274 K	P (bar)	Composition			Phase fraction		
		V	L <sub>w</sub>	H(II)	V	L <sub>w</sub>	H(II)
Propane	1	0.993593	0.000068	0.0	0.50319	0.49681	0.0
Water		0.006407	0.999932	0.0			
Propane	2	0.996866	0.000139	0.001005	0.50147	0.46351	0.03502
Water		0.003134	0.999861	0.998995			
Propane	3	0.998143	0.000215	0.001546	0.50029	0.09874	0.40097
Water		0.001857	0.999785	0.998454			

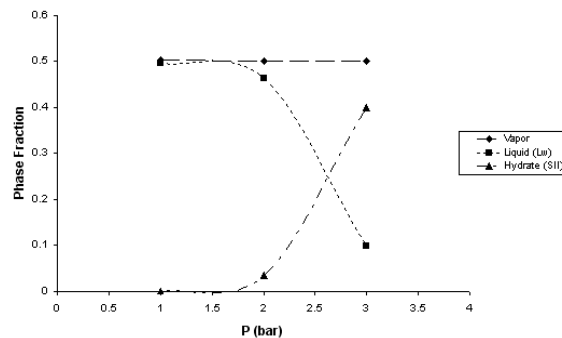


Fig 6. Changes of phase fraction versus pressure for propane-water system at 274 K

These calculations for propane-water system at 275 K temperature were performed and the results are shown as follow:

7.4. propane-water system at 275 K and composition (0.5,0.5)

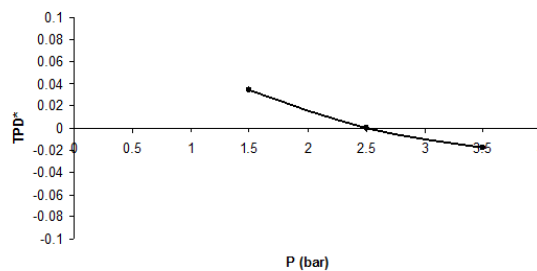


Fig 7. Changes of TPD\* function versus pressure for liquid phase of propane-water system at 275 K

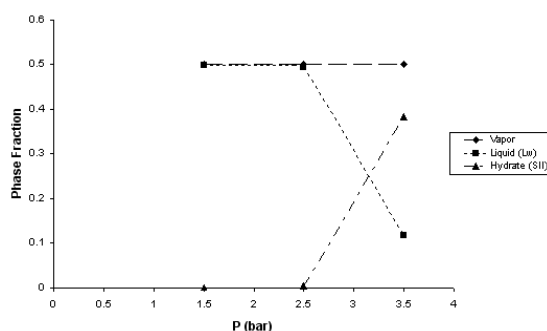


**Table 10.** The results of calculation of TPD\* function for liquid phase of propane-water system by using concentrations as a result of first step minimization as components composition in the new phase at 275 K

T = 275 K	Z <sub>1</sub>	Z <sub>2</sub>	TPD*			
			New liquid	Vapor	Hydrate I	Hydrate II
P = 2.5 bar	0.00062	0.99938	0.14763	- 0.01488	- 0.01058	0.02851
P = 3.5 bar	0.00068	0.99932	0.29511	- 0.02164	- 0.02721	0.05227

**Table 11.** Composition and phases fraction in equilibrium state for propane-water system at 275 K

T = 275 K	P (bar)	Composition			Phase fraction		
		V	L <sub>w</sub>	H(II)	V	L <sub>w</sub>	H(II)
Propane	1.5	0.995461	0.000099	0.0	0.50223	0.49773	0.0
Water		0.004539	0.999901	0.0			
Propane	2.5	0.997337	0.000169	0.001231	0.50124	0.49499	0.00377
Water		0.002663	0.999831	0.998769			
Propane	3.5	0.998143	0.000243	0.001769	0.50022	0.11712	0.38266
Water		0.001857	0.999757	0.998231			



**Fig 8.** Changes of phase fraction versus pressure for propane-water system at 275 K

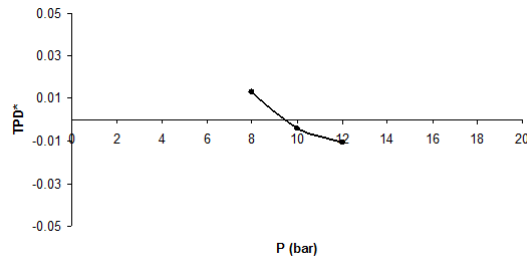
The results of comparison of equilibrium pressure of gas hydrate formation between TPD method and HWHYD model for propane-water system are shown in Table 12.

**Table 12.** Comparison of equilibrium pressure of gas hydrate formation in propane-water system between TPD method and HWHYD model

T (K)	P <sub>eq</sub> <sup>TPD</sup>	P <sub>eq</sub> <sup>HWHYD</sup>	% Error
274	1.7	1.9	10.5
275	2.5	2.4	4.1

**7.5. methane-methyl cyclo pentane-water system at 274 K and composition (0.05,0.05,0.9)**

The results of minimization of TPD function for liquid phase of methane-methyl cyclo pentane-water system are shown in Fig 9.



**Fig 9. Changes of TPD\* function versus pressure for liquid phase of methane-methyl cyclo pentane-water system at 274 K**

As a result of decomposition of liquid phase of methane-methyl cyclo pentane-water system, a new liquid and hydrate with structure H are formed. These results are shown in Table 13. The results of flash calculations for methane-methyl cyclo pentane-water system are displayed in Table 14. and Fig 10.

**Table 13. The results of calculation of TPD\* function for liquid phase of methane-methyl cyclo pentane-water system by using concentrations as a result of first step minimization as components composition in the new phase at 274 K**

T = 274 K	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>	TPD*				
				New liquid	Vapor	Hydrate I	Hydrate II	Hydrate H
P = 10 bar	0.00786	0.00091	0.99123	0.56786	- 0.05369	- 0.15277	- 0.13385	0.11799
P = 12 bar	0.01171	0.00099	0.98730	0.65845	- 0.08281	- 0.31227	- 0.15544	0.14090

**Table 14. Composition and phases fraction in equilibrium state for methane-methyl cyclo pentane-water system at 274 K**

T = 274 K	P (bar)	Composition			Phase fraction		
		V	L <sub>w</sub>	H(H)	V	L <sub>w</sub>	H(H)
Methane	8	0.499345	0.000166	0.0	0.09983	0.90017	0.0
MCP		0.499861	0.000109	0.0			
Water		0.000794	0.999725	0.0			
Methane	10	0.498279	0.000218	0.076713	0.09937	0.89682	0.00381
MCP		0.501103	0.000114	0.027404			
Water		0.000618	0.999668	0.895883			
Methane	12	0.429872	0.000249	0.076125	0.07869	0.70645	0.21486
MCP		0.569645	0.000120	0.025362			
Water		0.000483	0.999631	0.898513			

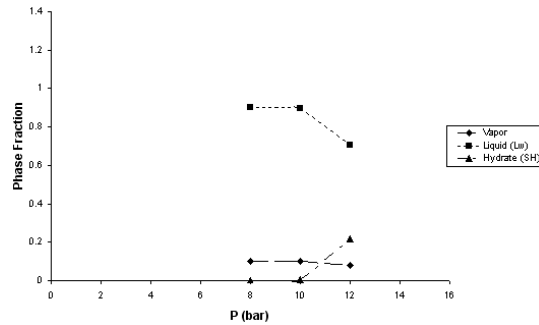


Fig 10. Changes of phase fraction versus pressure for methane-methyl cyclopentane-water system at 274 K

These calculations for methane-methyl cyclopentane-water system at 275 K temperature were performed and the results are shown as follow:

7.6. methane-methyl cyclopentane-water system at 275 K and composition (0.05,0.05,0.9)

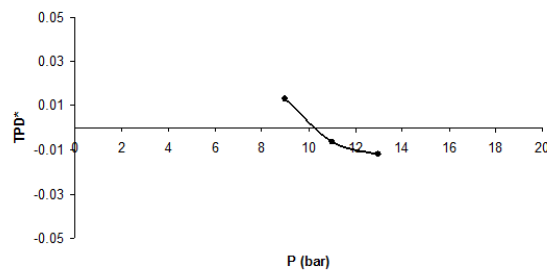


Fig 11. Changes of TPD\* function versus pressure for liquid phase of methane-methyl cyclopentane-water system at 275 K

Table 15. The results of calculation of TPD\* function for liquid phase of methane-methyl cyclopentane-water system by using concentrations as a result of first step minimization as components composition in the new phase at 275 K

T = 275 K	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>	TPD*				
				New liquid	Vapor	Hydrate I	Hydrate II	Hydrate H
P = 11 bar	0.00884	0.00087	0.99029	0.55977	- 0.05779	- 0.17406	- 0.14355	0.10358
P = 13 bar	0.01268	0.00099	0.98633	0.66030	- 0.07839	- 0.31875	- 0.15979	0.15092

Table 16. Composition and phases fraction in equilibrium state for methane-methyl cyclopentane-water system at 275 K

T = 275 K	P (bar)	Composition			Phase fraction		
		V	L <sub>w</sub>	H(H)	V	L <sub>w</sub>	H(H)
Methane	9	0.499288	0.000187	0.0	0.09980	0.90020	0.0
MCP		0.499962	0.000112	0.0			
Water		0.000750	0.999701	0.0			

Methane	11	0.496653	0.000243	0.080435	0.09883	0.89230	0.00887
MCP		0.502757	0.000113	0.025489			
Water		0.000590	0.999644	0.894076			
Methane	13	0.437069	0.000280	0.081207	0.08270	0.74462	0.17268
MCP		0.562463	0.000110	0.021899			
Water		0.000468	0.999610	0.896894			

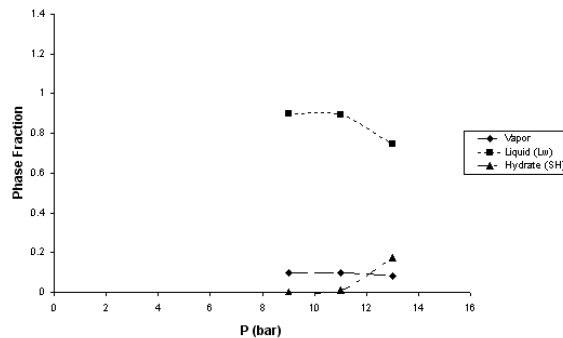


Fig 12. Changes of phase fraction versus pressure for methane-methyl cyclopentane-water system at 275 K

The results of comparison of equilibrium pressure of gas hydrate formation between TPD method and HWHYD model for methane-methyl cyclopentane-water system are shown in Table 17.

Table 17. Comparison of equilibrium pressure of gas hydrate formation in methane-methyl cyclopentane water system between TPD method and HWHYD model

T (K)	$P_{eq}^{TPD}$	$P_{eq}^{HWHYD}$	%Error
274	9.6	9.3	3.2
275	10.1	10.5	3.8

### 8. conclusions

In this work, TPD method for determination of conditions of gas hydrate formation is used. The results show that the vapor phase is always stable, but the liquid phase in certain temperature and specific pressure is unstable and decomposed. As a result of decomposition of unstable liquid phase two new phase, a new liquid and hydrate are formed. Subsequently, in order to determine the numbers and type of phases as a result of decomposition of liquid phase, with new concentrations as a result of first step minimization, TPD method is used again for any phase. Calculations for methane-water system with structure I, propane-water system with structure II and methane-methyl cyclopentane-water system with structure H are performed. Subsequently, for determination of amount and composition of phases in equilibrium state, multiphase flash calculations are performed.

### Acknowledgments

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### List of symbols

$C_{kj}$	Langmuir coefficient
$f_k$	fugacity of components in solid phase (SH)
$f_w^H$	fugacity of water in hydrate phase
$f_w^{MT}$	fugacity of water in empty lattice of hydrate
$f_{ij}$	fugacity of component i in phase j
$K$	chemical potential difference
$k$	dimensionless chemical potential difference
$K_{ij}$	distribution coefficient of component i in phase j
$NC$	number of component
$NP$	number of phase
$N_0$	number of empty cavities for any mole water
$n_{0j}$	fraction of empty cavity j
$P$	pressure
$TPD$	tangent plane distance, objective function
$TPD^*$	minimum of TPD function
$T$	temperature
$X_i$	mole number of component i
$x_i$	mole fraction of component i
$\bar{x}^*$	concentration that are minimize TPD function
$Z$	components composition of mixture
$\varphi_i$	fugacity coefficient of component i
$\mu_i$	chemical potential of component i

### References

- [1] E.G. Hammerschmidt, "Formation of Gas Hydrate in Natural Gas Transmission lines", Ind. Eng. Chem. , 26 (8), pp. 851-855, (1934).
- [2] J.H. Van der Waals and J.C. Platteuw, "Clathrate Solutions", Adv. Chem. Phys., pp. 1-57,(1959).
- [3] M.L. Michelsen, "The Isothermal Flash Problem", Part I. Stability, Fluid Phase Equilibria, 9, 21, (1982).
- [4] J.O. Valderrama, "A Generalized Patel-Teja Equation of State for Polar and Nonpolar Fluids and their Mixtures", J. Chem. Eng. Jpn. , 23(87), (1990).
- [5] D. Avlonitis, A. Danesh and A.C. Todd, "Prediction of VL & VLL Equilibria of Mixtures Containing Petroleum Reservoir Fluids & Methanol with a Cubic EOS", Fluid Phase Equilibria, vol. 94, pp. 181-216, (1994).
- [6] H. Behjati Rad, F. Varaminian, "Modeling of Stability Conditions in Phase Equilibria of Gas Hydrate", MSc Thesis, Department of Chemical Engineering, Gas and Petroleum, Semnan University, Iran, (2008).
- [7] M.L. Michelsen, "Calculation of Hydrate Fugacities", Chem. Eng. Sci., 46, (1991), pp. 1192-1193.
- [8] Heriot-Watt University Hydrate Model: <http://www.pet.hw.ac.uk>. See also: D. Avlonitis, "Thermodynamics of Gas Hydrate Equilibria", Ph.D. Thesis, Department of Petroleum Engineering, Heriot-Watt University, Edinburgh, UK, (1992).