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Review Article

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Methods of Predicting Hydrates Formation

Alireza Bozorgian[1,✉]

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ABSTRACT. Natural gas is one of the most important sources of energy supply in the current day and future and Iran is known as the second country with natural gas reserves. One of the main problems in the transfer of natural gas is the creation of hydrate in the pipelines and the blockage of these special lines in the cold seasons and cold areas of garlic. The aim of this study was to investigate the different conditions of natural gas hydrate formation and optimize MEG consumption to prevent hydrate formation. Gas hydrate is a crystalline compound formed by the trapping of gas molecules in cavities resulting from the hydrogen bonding of water. In the absence of a guest molecule (trapped gas) the cavity is dynamically unstable. However, if the guest gas molecule is placed inside these cavities, the non-polar bond formed between the gas and the water molecule will stabilize the structure and cause the hydrate to form at a temperature above the freezing point of the water. In this type of crystals, there is no chemical bond between the water molecules and the trapped gas molecules and the only factor in the stability of the crystals is the hydrogen bond between the host molecules and van der Waals force between the host and guest molecules.

Keywords: Hydrate; Energy; Natural gas; Hydrogen Bonding; Molecule.

INTRODUCTION

The design time of hydrate-related processes is the most basic issue in predicting the temperature and pressure at which hydrates are made. Manual computational methods are useful for quickly estimating the conditions of hydrates formation. Unfortunately, the disadvantage of these methods is that they are not accurate.[1] There are two common ways to quickly estimating the conditions of hydrates formation. Both of these methods are assigned to Katz and his colleagues. In order to separate these two methods, special letters of gas specific gravity and constant equilibrium k are used.[2, 3] The most important of these methods for predicting the temperature of gas hydrates formation are as follows:

Gas gravity method
Constant equilibrium method (*k*)
Trekell Campbell method
Baillie - Wichert method

GAS GRAVITY METHOD

The difference in equilibrium is the electromotive force behind the phenomenon. Obviously, the higher the electromotive force, the faster the phenomenon will occur. We know that to form a hydrate crystal, like other crystallization processes, nuclei must first form. To form nuclei, the gas concentration that is supposed to form the hydrate crystal must exceed its equilibrium in water and reach a super-saturated concentration. A three-phase equilibrium curve of hydrate formation for a gas has been symbolically shown. To form hydrates at a constant test temperature (T_{exp}), the equilibrium (P_{eq}) (point B) must be exceeded by increasing the pressure and reaching the value (P_{exp}) (point A). With this increase, the gas concentration pressure in the water will be higher than its equilibrium value at the temperature (T_{exp}) and the necessary ground will be provided for the nuclei formation.[4] In 1945, Katz introduced the most basic method of achieving the pressure and temperature of hydrate formation from a liquid-vapor compound (three-phase). In this method, the constant specific gravity lines in a temperature pressure diagram show the conditions under which the hydrate is made.[5, 6] To take advantage of this diagram shown in Fig. 1, the gas density is calculated first and by knowing one of the two

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✉ Corresponding author.
E-mail address: a.bozorgian@mhriau.ac.ir (A. Bozorgian)

[1] Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

concentrated factors of pressure or temperature, another concentrated factor is determined for the point of manufacture of the hydrate.[6]

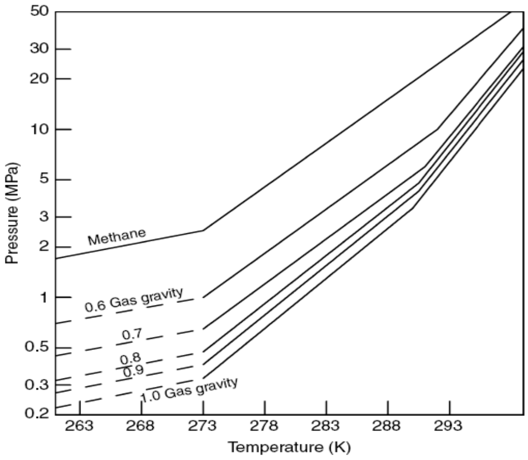

Fig. 1: Gas gravity curves in temperature - pressure to predict how hydrates are made.

CONSTANT EQUILIBRIUM METHOD (k)

The distribution coefficient method sometimes called the k-value method, was proposed by Carson, Katz and Wilcox. Carson and Katz defined a solid-steam distribution coefficient. As long as the pressure does not exceed 1000 psi, this method (equilibrium constant k) can be used. For natural gas and carbon dioxide components, K_{vsi} values are given as a function of temperature and pressure in Figs. 2-9.[7-10]

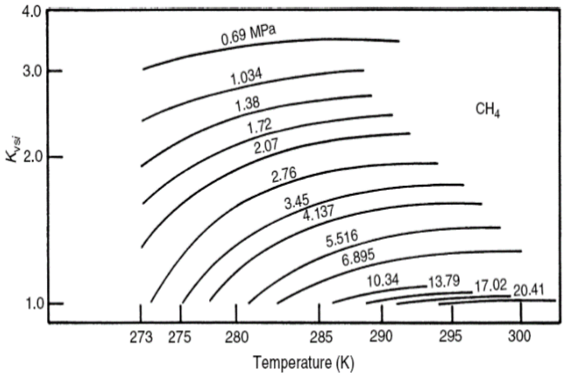

Fig. 2: K_{vsi} diagram for methane.

Eq. (1) replaces the values of K_{vsi} in Figs. 2-9 in the form of an algebraic expression. The factors are in Table 1.

$$Ln\,K_{vsi} = A + B*T + C + \Pi + D*T^{-1} + E*\Pi^{-1} + F*\Pi*T + G*T^{2} + H*\Pi^{2} + I*\Pi*T^{-1} + J*ln(\Pi*T^{-1}) + K*(\Pi^{-2}) + L*T*\Pi^{-1} + M*T^{2}*\Pi^{-1} + N*\Pi*T^{-2} + O*T*\Pi^{-3} + Q*T^{3} + R + \Pi^{3}*T^{-2} + S*T^{4} \tag{1}$$

Π = pressure is based on P_{Si} and T = temperature is based on degree Fahrenheit.

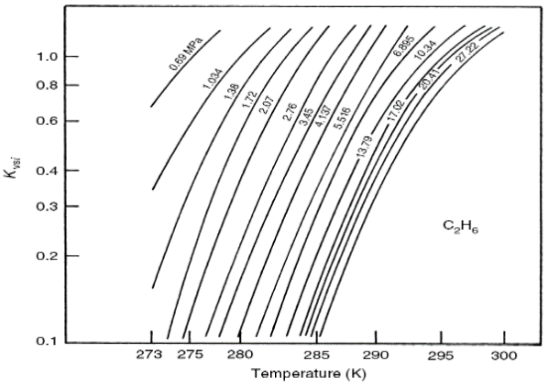

Fig. 3: K_{vsi} diagram for ethane.

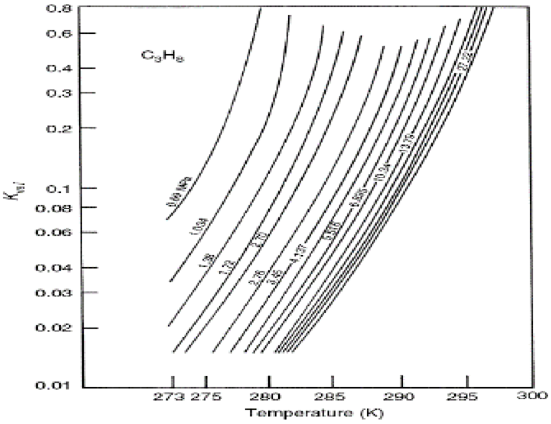

Fig. 4: K_{vsi} diagram for propane.

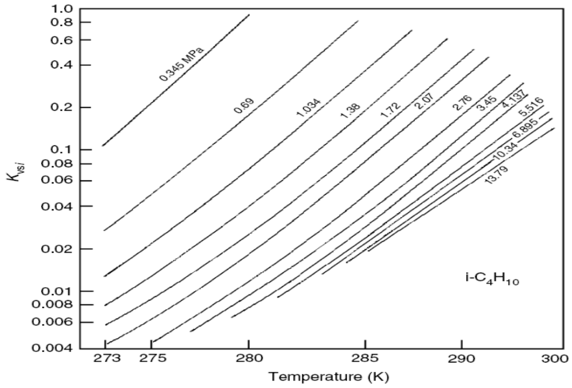

Fig. 5: K_{vsi} diagram for iso-butane.

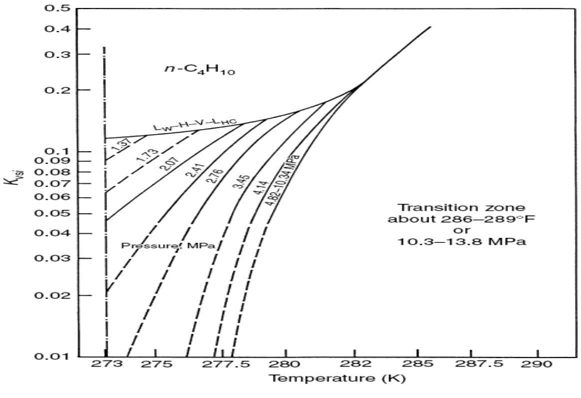

Fig. 6: K_{vsi} diagram for butane.

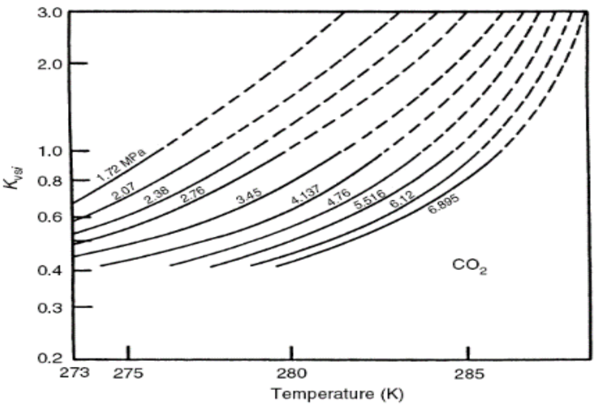

Fig. 7: K_{vsi} diagram for carbon dioxide.

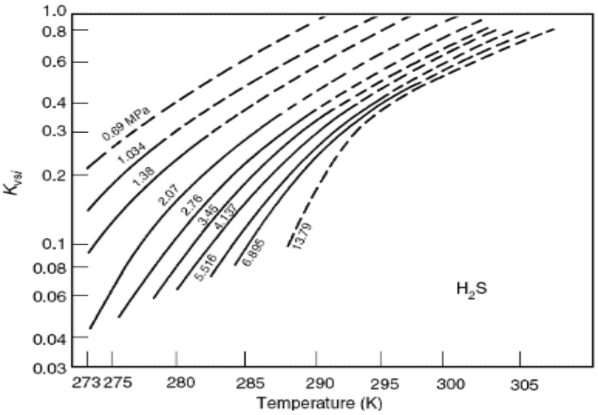

Fig. 8: K_{vsi} diagram for hydrogen sulfide.

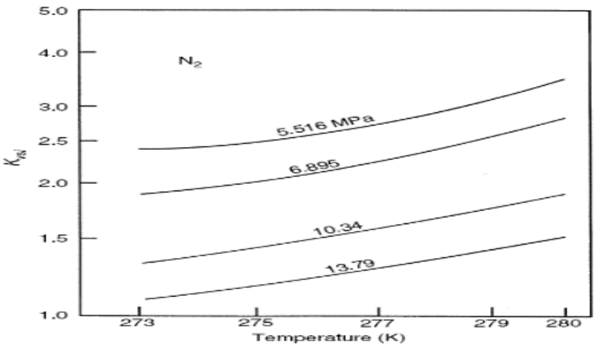

Fig. 9: K_{vsi} diagram for butane.

TREKELL CAMPBELL METHOD

This method is used to correct the Katz method and can be used with range pressure (1000-6000 psi). Campbell expressed his theory in 1978 that using the GPSA book formats at any pressure, the pure methane hydrate temperature and also in the gas by combining different percentage can be obtained the temperature of the hydrate formation and assumed that like C_5 and above, they play a negative role in the hydrate formation.[2, 11]

BAILLIE-WICHERT METHOD

Another graphical method for predicting hydrate was provided by Baillie-Wichert.

BAILLIE-WICHERT METHOD

Another graphical method for predicting hydrate was provided.

EXPERIMENTAL FORMULAS FOR DETERMINING HYDRATE FORMATION

According to the GPSA book, in order to avoid complex and tedious calculations to obtain data on the conditions of hydrate formation from the diagrams in the book, relationships for gases have been developed for when the density is known. The most popular experimental rules in hand based on gas density are Kobayashi, Berg and Motiee rules for calculation of hydrates formation conditions.[6, 12]

Based on the Katz-gas diagram, presented a fitting relation in terms of temperature (T), pressure (P) and specific gas density (γ_g) in three-phase equilibrium conditions to predict the temperature of hydrate formation, eq. (2).[13]

$$T = 1/[A_1 + A_2(\ln\gamma_g) + A_3(\ln P) + A_4(\ln\gamma_g)^2 + A_5(\ln\gamma_g)(\ln P) + A_6(\ln P)^2 + A_7(\ln\gamma_g)^3 + A_8(\ln\gamma_g)^2(\ln P) + A_9(\ln\gamma_g)(\ln P)^2 + A_{10}(\ln P)^3 + A_{11}(\ln P)^4 + A_{12}(\ln\gamma_g)^3(\ln P) + A_{13}(\ln\gamma_g)^2(\ln P)^2 + A_{14}(\ln\gamma_g)(\ln P)^3 + A_{15}(\ln P)^4] \quad (2)$$

The constant values of eq. (2) are given in Table 2.

This relation can be used in the temperature range of 34 to 60 ˚F, the pressure range of 65 to 1500 P_{sia} and the gas density range from 0.552 to 0.9.[14]

The relations of expansion with Berg is the explicit temperature which means that the temperature is calculated directly by having the pressure and density of the gas.[15] The relations for predicting the temperature of hydrate formation according to the size of the density are:

For when $0.555 \leq \gamma_g \leq 0.58$: (3)

And for when $0.58 \leq \gamma_g \leq 1.0$: (4)

MOTIEE RELATIONS

This relation is presented in two forms, explicit pressure and explicit temperature:

$$\log(P) = a_1 + a_2T + a_3T^2 + a_4\gamma_g + a_5\gamma_g^2 + a_6T\gamma_g \quad (5)$$

$$T = b_1 + b_2\log(P) + b_3(\log(P))^2 + b_4\gamma_g + b_5\gamma_g^2 + b_6\gamma_g\log(P) \quad (6)$$

Table 1: Constants of eq. (1).

Component	A	B	C	D	E	F
CH_4	1.63636	0.0	0.0	31.6621	-49.3534	$-5.31E^{-6}$
C_2H_6	6.41934	0.0	0.0	-290.283	2629.10	0.0
C_3H_8	-7.8499	0.0	00	47.56	0.0	$-1.17E^{-6}$
i-C_4H_{10}	-2.17137	0.0	0.0	0.0	0.0	0.0
n-C_4H_{10}	-37.211	0.86564	0.0	732.20	0.0	0.0
N_2	1.78857	0.0	-0.001356	-6.187	0.0	0.0
CO_2	9.0242	0.0	0.0	-207.033	0.0	$4.66E^{-5}$
H_2S	-4.7071	0.0	0.06192	82.627	0.0	$-7.39E^{-5}$

Component	G	H	I	J	K	L
CH_4	0.0	0.0	0.128525	-0.78338	0.0	0.0
C_2H_6	0.0	$-9.0E^{-8}$	0.129759	-1.19703	$-8.46E^{4}$	-71.0352
C_3H_8	$7.145E^{-4}$	0.0	0.0	0.12348	$1.669E^{4}$	0.0
i-C_4H_{10}	$1.251E^{-6}$	$1.0E^{-8}$	0.166097	-2.75945	0.0	0.0
n-C_4H_{10}	0.0	$9.37E^{-5}$	-1.07657	0.0	0.0	-66.221
N_2	0.0	$2.5E^{-7}$	0.0	0.0	0.0	0.0
CO_2	$-6.992E^{-3}$	$-2.89E^{-5}$	$-6.223E^{-3}$	0.0	0.0	0.0
H_2S	0.0	0.0	0.240869	-0.64405	0.0	0.0

Component	M	N	O	Q	R	S
CH_4	0.0	-5.3569	0.0	$-2.3E^{-7}$	$-2.0E^{-8}$	0.0
C_2H_6	0.596404	-4.7437	$7.82E^{4}$	0.0	0.0	0.0
C_3H_8	0.23319	0.0	$-4.48E^{4}$	$5.5E^{-5}$	0.0	0.0
i-C_4H_{10}	0.0	0.0	$-8.84E^{2}$	0.0	$-5.4E^{-7}$	$-1.0E^{-8}$
n-C_4H_{10}	0.0	0.0	$9.17E^{5}$	0.0	$4.98E^{-6}$	$-1.26E^{-6}$
N_2	0.0	0.0	$5.87E^{5}$	0.0	$1.0E^{-8}$	$1.1E^{-7}$
CO_2	0.27098	0.0	0.0	$8.82E^{-5}$	$2.55E^{-5}$	0.0
H_2S	0.0	-12.704	0.0	$-1.3E^{-5}$	0.0	0.0

Table 2: Constants of eq. (2).

Constant values	Constant values
$A_1 = 2.7707715\times10^{-3}$	$A_9 = -2.3279181\times10^{-4}$
$A_2 = -2.782238\times10^{-3}$	$A_{10} = -2.6840758\times10^{-3}$
$A_3 = -5.649288\times10^{-4}$	$A_{11} = 4.6610555\times10^{-3}$
$A_4 = -1.298593\times10^{-3}$	$A_{12} = 5.5542412\times10^{-4}$
$A_5 = 1.407119\times10^{-3}$	$A_{13} = -1.4727765\times10^{-5}$
$A_6 = 1.785744\times10^{-3}$	$A_{14} = 1.3938082\times10^{-5}$
$A_7 = 1.130284\times10^{-3}$	$A_{15} = 1.488501\times10^{-6}$
$A_8 = 5.928235\times10^{-4}$	

HAMMERSCHMIT RELATION

Hammerschmit presented the temperature formula for hydrates formation as follows:

$$T = \alpha P^{\beta} \tag{7}$$

Table 3: Constant of eq. (7)

Coefficients	Coefficient Values	Standard Error
α	14.7593	2.471904×10^{-1}
β	0.2101	6.299044×10^{-2}

Obtain the pressure of hydrates formation based on gas density. The equation is as follows:[16]

$$\log P = \beta + 0.497(t + kt^2) + 1 \tag{8}$$

$$\beta = 2.681 - 3.811\gamma + 1.679\gamma^2 \tag{9}$$

$$K = -0.006 + 0.011\gamma + 0.011\gamma^2 \tag{10}$$

Obtained the following equation by manual calculations to determine the temperature of hydrate formation by density and gas pressure.[17]

$$T = 13.47\ln(P) + 32.47\log(\gamma) - 1.675\ln(P)\ln(\gamma) - 20.35 \tag{11}$$

QSTERGRAAD RELATION

The equations were proposed by Custer Gard and colleagues who began their research with a relatively simple function of hydrate formation conditions using a, gas gravity method which is used only for sweet gases.

$$\ln p = (c_1(\gamma + c_2)^{-3} + c_3 F_m + c_4 {F_m}^2 + c_5)T + c_6(\gamma + c_7)^{-3} + c_8 F_m + c_9 {F_m}^2 + c_{10} \qquad (12)$$

The constants of eq. (12) are given in Table 4.[18]

Table 4: Constant of eq. (12)

C₁	4.5134 E^{-3}	**C₆**	3.6625E^{-4}
C₂	0.46852	**C₇**	-0.485054
C₃	2.18636 E^{-2}	**C₈**	-5.44376
C₄	-8.417 E^{-2}	**C₉**	3.89E^{-3}
C₅	0.129622	**C₁₀**	-29.9351

HYDRATE$^+$ SOFTWARE

This software is used to predict the conditions of hydrates formation for gas compounds and it has the ability to determine the temperature of hydrate formation at different pressures and the pressure of hydrate formation at different temperatures with the combination of gas mixing percentage. In Hydrate Plus (Hydrate$^+$) calculations are made by Mann et al. or the Baillie-Wichert method.[19-22]

DWHC-HWU SOFTWARE

The Distilled Water-Hydrate Correlation–HWU software was developed by Tohidi at the University of Herat Watt and is mostly used to calculate the conditions of hydrates formation in hydrocarbon tanks. In this software, H_2S component is not considered and in this study, its values are presented in terms of CO_2 component.[23-25]

CONCLUSION

Gas hydrates are formed in systems that include water and gas, the network of water molecules (host molecules) traps paraffin such as methane, ethane, propane, iso-butane, carbon dioxide, etc. (guest molecules) at low temperatures and high pressures in their cavities. Gas hydrates are non-stoichiometric solids that look similar to ice (or snow) but are completely different in structure. Water molecules in the structure of hydrates, like the structure of ice, form hydrogen bonds together and create hollow (cage-like) and instability cavities. Hydrates are formed at specific temperatures and pressures and in the presence of gas molecules proportional to the size of the cages. There is no chemical interaction between guest molecules and the structure formed by water molecules and only by the interaction of physical forces (van der Waals forces) between the trapped gases and the host molecules does the structure of the hydrates become stable, so the hydrates are classified as clathrate. In the industry, attention to gas hydrates began when the hydrate formation in pipelines blocked the flow path and eventually cut off service and stopped production. In this regard, Iran is one of the countries that have rich natural gas reserves. The hydrates formation in natural gas transmission pipelines increases the flow pressure drop, blocking the path and sometimes exploding the flow transmission pipeline. Thermal exchangers are one of the most practical equipment in the oil and gas industry, especially NGL PLANTS. Clathrate consists of a combination of a number of host molecules and one or more guest molecules that the stability of these compounds depends entirely on the presence of both components. The general formula for M_nH_2O gas hydrates is that M represents guest molecules. The hydrate formation process has exactly the same steps as the crystallization process and involves two stages of nucleation and growth. Studies have shown that hydrate crystals do not form quickly if the necessary conditions are met but it takes some time for the necessary formation to take place between the water molecules then cages are formed which this time is called induction time. In addition to classifying hydrates based on their constituent structures, there is a second type of classification for hydrates in which hydrates are evaluated based on guest molecules.

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