Kinetics of Propane Hydrate Formation in Agitated Reactor: A Mass Transfer Approach

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ARTICLE INFO	ABSTRACT
	Understanding the kinetics of gas hydrate formation is essential to model and predict the hydrate formation (or dissociation) process. In the present paper, we investigated the formation of pure propane gas hydrate as a former gas. In this regard, several experiments were conducted to measure the rate of hydrate formation under various pressures (410 to 510 kPa) and temperatures (274 K to 277 K) in a controlled temperature stirred reactor. It was observed that propane consumption rate can be assumed constant with time. Mass transfer approach was used to estimate the mass transfer coefficient in the gas-liquid contact area as a function of pressure and temperature. Results indicated that mass transfer approach can predict the kinetics of propane hydrate formation. In other words, it is reasonable to assume that this process is a mass transfer limited phenomena and in the mass transfer in the liquid side the gas-liquid contact area controls the hydrate growth.

1. Introduction

Clathrate hydrates are crystalline compounds that are formed from guest molecules and host water molecules under suitable conditions of temperature and pressure. The water molecules are linked together with hydrogen bonds and form a three-dimensional structure containing cavities capable of entrapping guest molecules [1]. Depending on the size and chemical characteristics of gas molecules, natural gas can form two types of hydrate structures (Structures I and II) [2].

Historically, gas hydrates have been investigated to deal with flow assurance issues during natural gas production and transportation [3]. The oil and gas industry spends over $200 M annually to prevent hydrate formation to maintain flow assurance [4]. Today, several applications have been proposed that have rendered gas hydrate phenomenon as a promising technique. The application of gas hydrates in carbon dioxide sequestration, hydrate based gas separation processes (HBGS) and natural gas storage and transportation has intrigued many researchers over the past years [5]. Moreover, huge sources of natural-gas hydrate have been discovered and considerable efforts have been made towards the production of this type of resource [6]. Understanding the kinetics of

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hydrate formation is necessary insofar as the mentioned applications are concerned. Riberio and Lage provided an extensive historical and theoretical framework for modeling of gas hydrate kinetics [7]. Several researchers have attempted to discover and predict hydrate formation, among whom Vysniauskas and Bishnoi were the first ones to attempt to measure the rate of methane hydrate formation [8]. Based on the crystallization kinetic and mass transfer effect, Englezos et al. developed a model to predict the formation kinetics of methane and ethane hydrates [9]. Gillard et al. proposed an empirical correlation based on the work of Englezos et al. [10]. Monfert et al. also proposed a semi empirical model with fugacity and driving force taken from Englezos et al. and Vysnauskas and Bishnoi, respectively [11]. According to Clarke and Bishnoi, Englezos et al.'s model is only valid for low supersaturated systems due to the assumption of negligible primary crystallization after nucleation [12]. Skovberg and Rasmusen simplified Englezos model to mass transfer limited model where they assumed that the most important step in gas diffusion through water is gas-liquid interface mass transfer which controls the hydrate formation kinetics [13]. Most of the theoretical and experimental studies were carried out to illustrate that hydrate formation and growth mechanism were inherently complex and system dependent.

Propane as a hydrate forming compound plays an important role in the study of production of natural gas from gas hydrate reservoirs and hydrate based gas separation (HBGS). Because the propane only participates to form structure II, the presence of small amount of propane in mixture reduces the equilibrium pressure significantly.

Bergeron and Servio [14] studied the hydrate formation of propane based on the model proposed by Englezos et al. [9]. Their modelling includes three steps of mass transfer and hydrate reaction coupled with population balance theory but in the current work, we assumed that the mass transfer controls the rate of hydrate formation. Recently, Mohebbi and Behbahani studied the multicomponent gas hydrate formation and developed individual mass transfer coefficients (MTC) for each component (including propane) [15]. Because the hydrate formation reaction takes place in the gas-liquid interface (in addition to the bulk of the aqueous phase), the calculated mass transfer coefficient is enhanced mass transfer coefficient and is affected by the reaction of hydrate formation. In addition, the formation reaction is affected by some parameters such as concentration of compounds that is determined by the pressure and temperature. As their work was concentrated on natural gas mixture at high pressure, the calculated mass transfer coefficient can be different from the case of pure propane.

In this work, the kinetic of gas hydrate formation from propane was investigated. Several isobaric and isothermal experiments were conducted to determine the rate of propane consumption. The model proposed by Mohebbi et al. (an extension of Skovberg and Rusmsen's Model - [13]) was used to determine the mass transfer coefficient during gas hydrate formation [16]. The objective of this work was to investigate the ability of the mass transfer limited model to predict MTC of propane hydrate.

2. Theory
Several kinetic models have been proposed regarding the kinetics of hydrate formation

and dissociation [7]. The general formulation of the kinetic model to describe hydrate formation and dissociation can be expressed as follows [17]:

$$\frac{dn_H}{dt} = A_S k \, e^{-\frac{\Delta E}{RT}} \left(f_g - f_{eq} \right) \qquad (1)$$

where n_H, t, A_S are amount of consumed gas (molar) by the hydrate phase, time and solid phase area, respectively. k, ΔE and f represent kinetic model constant, activation energy and fugacity. Subscript g and eq are referred to gas and equilibrium states. Because the solubility of propane in water is very low, the gas phase resistance can be ignored [18]. Consequently, f_g can be replaced by f_i and Eq. 1 becomes:

$$\frac{dn_H}{dt} = A_S k e^{-\frac{\Delta E}{RT}} \left(f_i - f_{eq} \right) \qquad (2)$$

where f_i is the fugacity at the interface.

Henry's law can be used for low soluble gas in the aqueous phase.

$$\frac{dn_H}{dt} = A_S k e^{-\frac{\Delta E}{RT}} \left(H_i x_i - H_{eq} x_{eq} \right) \qquad (3)$$

It can be assumed that at low and moderate pressure conditions, the Henry's law constant is independent on pressure [19]. Thus:

$$\frac{dn_H}{dt} = A_S k e^{-\frac{\Delta E}{RT}} H \left(x_i - x_{eq} \right) \qquad (4)$$

where H is the Henry's law constant. According to the mass transfer approach model [13 and 16], the gas consumption rate does not depend on the surface area of the hydrate particles, and it is controlled by the mass transfer at the gas-water contact area. In other words, A_S is replaced with the contact area between the gaseous and aqueous phases (A_{V-L}) [17]. Consequently, at constant temperature, Eq. 4 is given by:

$$\frac{dn_H}{dt} = A_{V-L} k e^{-\frac{\Delta E}{RT}} H \frac{C_W}{C_W} \left(x_i - x_{eq} \right) = A_{V-L} C_W \frac{k e^{-\frac{\Delta E}{RT}} H}{C_W} \left(x_i - x_{eq} \right) = A_{V-L} C_W k_L \left(x_i - x_{eq} \right) \qquad (5)$$

where k_L is defined mass transfer coefficient (MTC) and is presented by the following equation:

$$\frac{k e^{-\frac{\Delta E}{RT}} H}{C_W} = k_L \qquad (6)$$

In the above equation, k_L and C_W are the mass transfer coefficient at the vapour-liquid interface and water concentration, respectively.

Another systematic approach to investigate the kinetics of hydrate formation is to consider all possible resistances to hydrate growth and then evaluate the most important resistance(s) among others. The hydrate

formation process can be described by five resistances (stages):

- Mass transfer from the gas bulk to the gas–water interface
- Mass transfer from the gas–water interface (interface diffusional layer)
- Gas molecule transfer in the bulk of aqueous phase
- Mass transfer around the hydrate particle (particle diffusional layer)
- Hydrate formation reaction (it is common to assume a first order reaction in literature)

Because gas hydrate formers are low soluble gases in water, it is reasonable to

ignore the mass transfer resistance (step 1) in the gas phase [18]. To investigate the hydrate kinetics experimentally, it is usual to provide a homogeneous liquid (aqueous) phase with adequate mixing. As a result, it is convenient to eliminate the mass transfer resistance in the bulk of liquid (step 3). Adequate mixing also provides isothermal conditions and thus removes thermal resistance during experiment.

The developed kinetic model by Englezos et al. is based on crystallization theory and considers steps 2, 4 and 5 [9]. The overall resistance to hydrate growth can be presented by:

$$R = \frac{1}{A_P}\left(\frac{1}{k_D} + \frac{1}{k_R}\right) + \frac{1}{A_{V-L}}\frac{1}{k_L} \qquad (7)$$

where A_P is the total solid area (hydrate particle), k_D the mass transfer coefficient in the discussion layer around the hydrate particles, k_r is the first order reaction constant.

To determine the mass transfer coefficient around the particles (k_D), Herri et al. [20] and Bergeron and Servio [14] used analogy correlations based on Sherwood dimensionless number for solid particles in an agitated vessel. Bergeron and Servio, used the following correlation to estimate k_L:

$$Sh = \frac{k_D L}{D} = 2 + 0.6\,\mathrm{Re}^{0.5}\,Sc^{0.33} \qquad (8)$$

where D is the gas diffusivity in water and L is the particle diameter of gas hydrate. They estimated that the value of k_D is approximately in the order of 10^{-5} m/s. Then, they compared it to kr which had been previously measured by Clark and Bishnoi to be in the order of 10-8 m/s [12]. They concluded that $1/k_D$ is negligible to $1/k_r$. Therefore, Eq. 7 is given by:

$$R = \frac{1}{A_P}\frac{1}{k_r} + \frac{1}{A_{V-L}}\frac{1}{k_L} \qquad (9)$$

Therefore, Bergeron and Servio [14] used the following equation to predict the number of consumed moles for hydrate growth:

$$\frac{dn}{dt} = \frac{C_W\left(x_i - x_{eq}\right)}{\dfrac{1}{A_P}\dfrac{1}{k_r} + \dfrac{1}{A_{V-L}}\dfrac{1}{k_L}} \qquad (10)$$

They used mole fraction as the driving force that was previously proposed by Hashemi et al. [21]. In the above equation C_W is the concentration of water in the aqueous phase.

Like other crystallization processes, A_P increases as the process continues. According to Eq. 9, increase in total particle area accelerates the gas consumption rate. But there are some studies which illustrate the gas consumption rate is relatively constant [1, 8, 9, 14, 22]. An explanation of this observation is that the rate of gas uptake by the hydrate phase is not a function of particle size and numbers. In other words, the first term on the right side of Eq. 9 (hydrate reaction resistance) is negligible compared to second term (mass transfer resistance in the gas-liquid interface). As a result, Eq. 10 can be converted to the following equation which is similar to Eq. 5:

$$\frac{dn}{dt} = A_{V-L}k_L C_W\left(x_i - x_{eq}\right) \qquad (11)$$

To determine x_i and x_{eq}, Henry's law was used:

$$P\varphi^v y = Hx \qquad (12)$$

where φ and y are the fugacity coefficient and composition in the gas phase, respectively. Equation 13 was used to estimate the Henry's law constant of propane [23].

$$H = 100 \times \exp(-22.61 + 0.1893(T) - 0.00026(T^2) + 0.6189 \times 10^{-6}(\frac{P}{R})) \qquad (13)$$

In which, R is universal gas constant (8.314×10^{-3} kJ/mole.K) and H and P are in kPa. SRK equation of state was used to determine the fugacity in the gas phase [24]. x_i and x_{eq} were calculated at T, P_{op} (operation pressure) and T, P_{eq} (equilibrium pressure) respectively. Experimental data were employed to accurately predict the equilibrium conditions of propane hydrate formation [2]. A third order polynomial equation properly presents the equilibrium pressure as a function of temperature (Eq. 14 – see Fig. 2).

$$P_{eq}(kPa) = 1.38181(T^3) - 1134.7405(T^2) + 310660.4498(T) - 28353915.2 \qquad (14)$$

3. Experimental Apparatus

The details of the Apparatus are shown in Fig. 1. The system is the same as that proposed by Naseh et al [25]. The setup consists of a double-wall stirred visual reactor made of Stainless Steel 316 (440 mL). A 4cm star coated magnetic bar is located in the cell and is rotated by an external magnetic stirrer (Labinco L-71). Smart Sensor Digital Tachometer is used to calibrate the stirrer. The heat is removed from the cell by a bath circulator (Sahand Azar) that provides cooling media in the jacket of the cell. Two temperature indicators (PT100) are located in the reactor to measure the temperature. These PT100 indicators were calibrated against standard resistance (temperature uncertainty, ± 0.1 K). The cell pressure was measured by a SENSYS pressure transmitter with an accuracy of 5 kPa and was checked by an Achcroft pressure gauge (pressure uncertainty, ± 1 kPa). A Ruska pump kept the cell pressure constant using gas injection with the accuracy of 0.01×10^{-6} m^3. All experiments were carried out at 300 rpm. It turned out, when the stirring rate was lower than 250 rpm, the hydrate phase would form a layer on the gas-liquid interface, and the magnetic bar would be unable to provide a uniform mixture. On the other hand, when the stirring rate was more than 400rpm, the surface would get rippled and considerable bubbles would be observed.
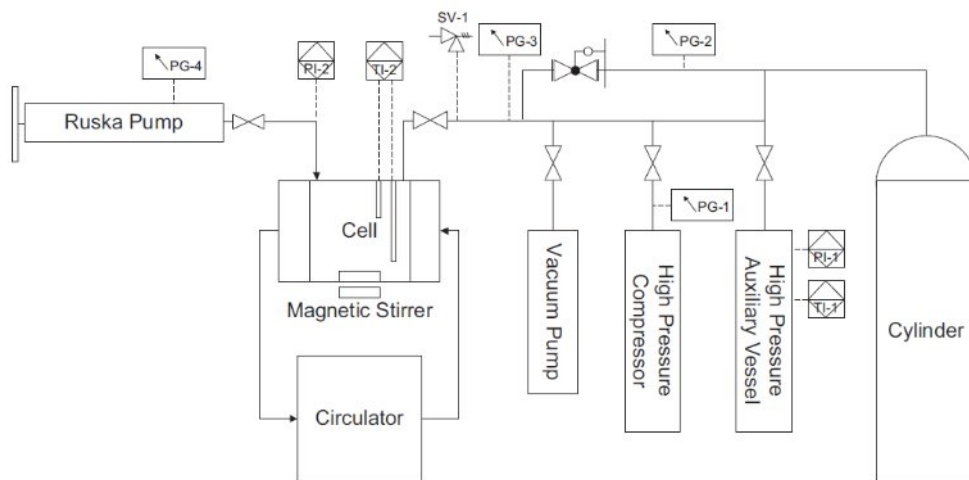

Figure 1. Experimental apparatus to determine gas consumption rate in isobaric condition. TI: temperature indicator; PI: pressure indicator; PG: pressure gage; SV: safety valve.

4. Procedure

All experiments were conducted at constant temperature and pressure (isobaric and isothermal condition). Prior to any water injection, the reactor cell was vacuumed two times to strip the aqueous phase from any dissolved gas. 90 mL of highly purified fresh distilled water was injected into the cell. The cell was then pressurized with pure propane (below hydrate equilibrium pressure) and cooled down to the desired temperature. The propane was provided by Persian Gas Corporation with the purity of 99.95 %.

Next, the cell pressure was gradually pressurized. The stirrer was maintained at low speed (less than 100 rpm) to allow an isothermal condition in the cell. When the operation pressure was reached, the stirrer speed was set to 300 rpm. As the hydrate began to form, the Ruska pump provided the constant pressure by injecting sufficient gas. The injected gas was recorded every 30 s. The volume of injected gas (consumed by the hydrate phase) was converted to mole through the following equation:

$$n_H = \frac{P_{op} \times V_{inj}}{Z \times R \times T_{room}} \qquad (15)$$

where V_{inj} represents the amount of propane injected to the cell by the Ruska pump, and Z is the compressibility factor estimated by SRK equation of state at T_{room} and P_{op}. Room temperature was recorded in each experiment by a digital temperature indicator with an accuracy of 0.1 K. All experiments were conducted between hydrate equilibrium and vapour pressure [26] region as illustrated in Fig. 2. In order to determine the gas-liquid interface, some pictures were taken at 250 rpm, 300 rpm and 350 rpm with CCD camera - SONY. The CCD camera was connected to a personal computer to provide recording and taking snapshots. As the camera had the capacity of taking High Definition (HD) pictures the accuracy of photos was reliable. Each picture was then digitized, and the gas-liquid interface area was estimated with numerical integration (Table 1). The uncertainty of estimated area was found about 10^{-5} m^2.
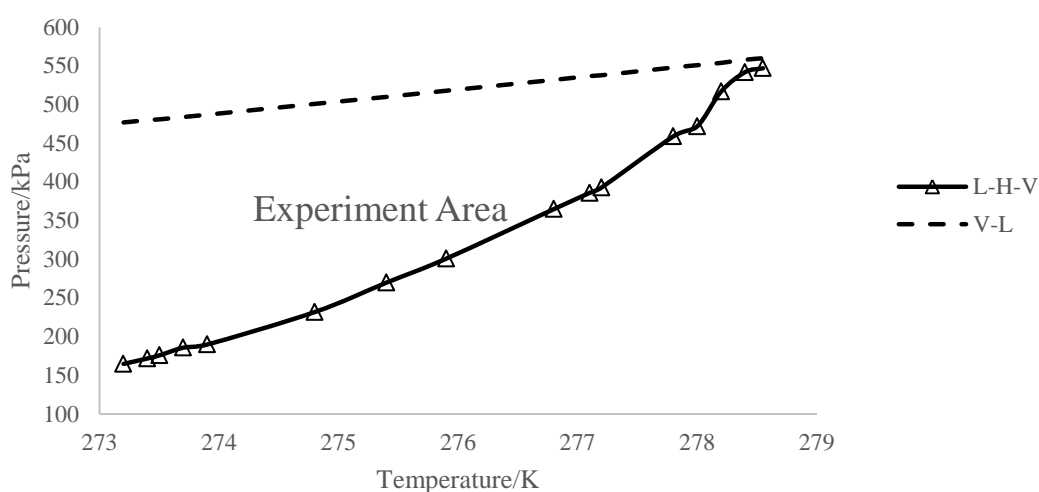

Figure 2. Hydrate equilibrium and vapour pressure curves of propane – V-L [26] and L-H-V [2].

Table 1

Gas-liquid interfacial area in different rpm.

rpm	$A_{V-L} \times 10^4$ m^2
250	29.9
300	31.2
350	32.4

5. Results and Discussion

Seven isobaric tests were conducted at 3 different temperatures (274.2, 275.2 and 277.2 K). Figures 3-5 illustrate the amount of consumed gas. It was observed that about 30 min after hydrate growth, a relatively thick hydrate layer formed in the gas-liquid interface and prevented free diffusion of propane to the liquid bulk. Consequently, all experiments were limited to about 30 min after growth time.

The slope of the curves shows the rate of gas uptaken by the gas hydrate (Fig. 3-5). As it is illustrated, the consumed gas is fairly linear with time, meaning the gas consumption rate remained relatively constant, an observation that can be explained through the mass transfer limited theory. As it was predicted, at higher pressures the rate of gas consumed by the hydrate growth is higher than lower pressures.
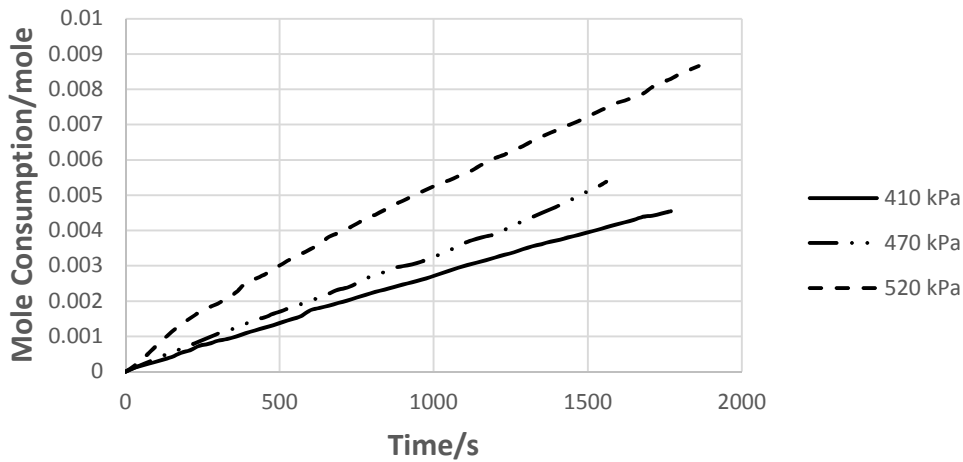

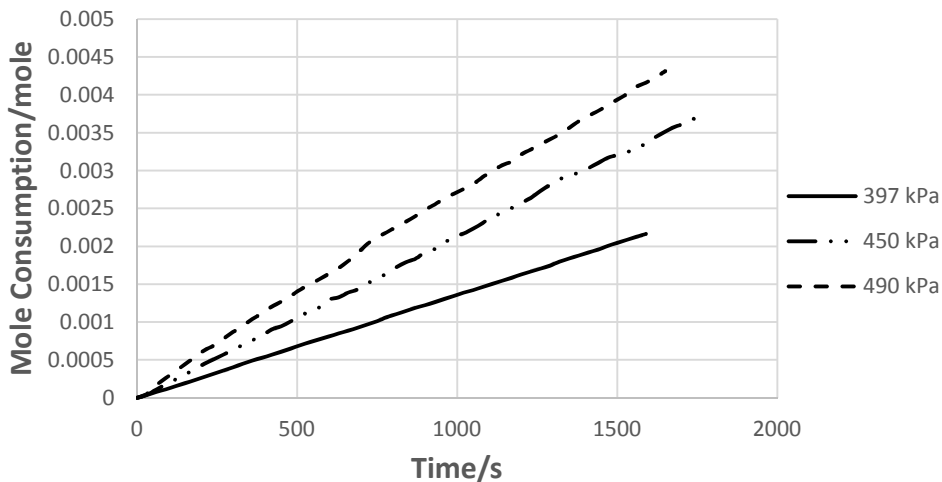**Figure 3.** Mole consumption during hydrate growth at 274.2 K and 300 rpm.

Figure 4. Mole consumption during hydrate growth at 275.2 K and 300 rpm.
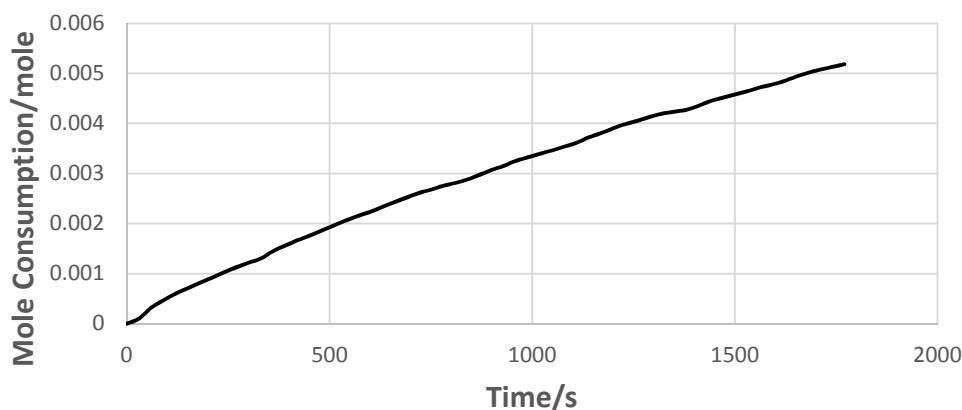
Figure 5. Mole consumption during hydrate growth at 277.2 K, 510 kPa and 300 rpm.

The mass transfer coefficients (k_L) were calculated according to Eq. 5 and are listed in Table 2. The increase in k_L is the result of a higher pseudo-reaction in the contact area of gas and liquid. In other words, the rise in the pressure of the system (at constant temperature) leads to higher degrees of super-saturation in the system and consequently higher hydrate formation in the gas-liquid area. Moreover, uncertainties of the mass transfer coefficients are listed in Table 2. In addition, two more experiments were carried out to ensure reproducibility of data at 274.2 K and 470 kPa. Results were in the range of uncertainty that indicate reproducibility of method.

Although some trends can be assumed as higher order (Fig. 2, at P = 520 kPa and Fig. 5, at P = 510 kPa). It is reasonable to assume they are linear. In other words, the mass transfer model can predict the rate of gas consumption with an acceptable accuracy. The main advantage of mass transfer model is its simplicity among other models.

Calculated k_L (Table 2) shows that MTC is affected by pressure, a finding confirmed by certain researches in the literature [16, 25]. To show the effect of pressure and temperature on mass transfer coefficient a second polynomial equation was used (higher order equation had no major improvement in the regression results). Equation 16 gives the relationship among mass transfer coefficient, temperature and pressure.

$$k_L(m/s) = \left[a + b\frac{T-T_{mean}}{T_{STD}} + c\frac{P-P_{mean}}{P_{STD}} + d\left(\frac{T-T_{mean}}{T_{STD}}\right)^2 + e \times \frac{P-P_{mean}}{P_{STD}} \times \frac{T-T_{mean}}{T_{STD}} \right] \times 10^{-4} \qquad (16)$$

where P is in kPa. Equation 16 was presented in the form of normalized equation to show the role of each variable (temperature and pressure). T_{mean}, T_{STD}, P_{mean} and P_{STD} are mean value and standard deviation of temperature and pressure respectively. The

equation's constants were listed in Table 3. SSE and RSME are summed square of residuals and root of mean square error, respectively. Just as with SSE, an MSE value closer to 0 indicates a fit that is more useful for prediction.

Equation 16 shows that the mass transfer coefficient increases with increase in both temperature and pressure.

Table 1
Calculated k_L at different temperature and pressure.

Experiment number	T / K	P / kPa	H / 100 kPa	ϕ^V	$k_L \times 10^4$ / m/s	Uncertainty $\times 10^6$ / m/s
1	274.2	410	17606	0.9766	1.479	7.18
2	274.2	470	17684	0.9634	1.523	7.41
3	274.2	520	17750	0.9525	1.760	8.58
4	275.2	397	18425	0.9802	1.195	5.73
5	275.2	450	18498	0.9687	1.416	6.81
6	275.2	490	18553	0.9601	1.440	6.94
7	277.2	510	20360	0.9578	3.712	15.4

Table 2
Constants of Equation 16.

a	b	c	d	e	R^2	SSE	RMSE
1.374	0.1286	0.1276	0.4815	0.01123	0.9972	0.01232	0.0785

The same method and procedure was used for multicomponent by Mohebbi and Behbahani [15]. In their work, the mass transfer coefficients of hydrate formers (including propane) in natural gas were measured and reported. The gas hydrate structure of both works was of type II. The magnitude of both mass transfer coefficients was 10^{-4} m/s.

6. Conclusions

Hydrate kinetics is affected by two mechanisms. The first is the gas transport from the gas phase to the liquid bulk, and the second is the kinetics of the hydrate particle. The former is constant during hydrate formation while the latter changes due to the size and number of particles. These two processes result in gas consumption by the hydrate particles. The mass transfer approach explains the fact that the particles kinetics is negligible compared with the mass transfer in the gas-liquid interface.

In this study, several experiments were conducted so as to investigate the kinetics of propane hydrate. All experiments were carried out at constant temperature and pressure in a stirred reactor. Gas consumption rates were calculated and were found to be relatively constant. Since particle kinetics varies with time and the total kinetics of the system remains unchanged, it was concluded that particle kinetics has no major effect on the hydrate formation. Consequently, it can be assumed that this process is a mass transfer limited phenomena and the mass transfer in the liquid side of the gas-liquid contact area controls the hydrate growth. Furthermore, mass transfer coefficient was determined in each experiment and was found to be dependent on pressure and temperature. It should be noted that this conclusion is only valid following turbidity point and for systems with adequate mixing. More studies should be conducted regarding the effect of hydrate formation reaction on the mass transfer coefficient.

Nomenclature

A	area [m^2].
C	concentration [mole/m^3].
D	gas diffusivity [m^2/s].
f	fugacity [kPa].
k	mass transfer coefficient [m/s].
H	Henry's law constant [kPa].
L	particle diameter [m].
MTC	mass transfer coefficient [m/s].
n	mole [mole].
P	pressure [kPa].
R	universal gas constant [J/mole.K].
t	time [s].
T	temperature [K].
x	mole fraction in liquid phase.
y	mole fraction in vapour phase.
Z	compressibility factor.
φ	fugacity coefficient.

Superscript

V	vapour phase.

Subscript

eq	equilibrium.
g	gas.
H	hydrate.
i	interface.
inj	injected.
L	liquid.
Mean	mean value.
op	operating conditions.
room	room conditions.
STD	standard deviation.
V-L	vapour, liquid area.
S	surface of mass transfer.
W	water.

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