MODELING OF METHANE AND PROpane HYDRATE FORMATION KINETICS BASED ON CHEMICAL AFFINITY

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ABSTRACT
In this study, experimental data on the kinetics of methane and propane hydrate formation at constant volume were collected. The experiments were carried out in a batch reactor at different temperatures and pressures. The chemical affinity was used for the modeling of hydrate formation rate in a constant volume process. In this method, the system was considered as classical thermodynamic or macroscopic view. The results show that this method can predict constant volume experimental data well for both crystals I and II hydrate former.

Keywords: Chemical affinity, Methane, Propane, Formation kinetics, Gas hydrates

INTRODUCTION
Gas hydrates are crystalline solids. They are composed of polyhedra of hydrogen bonded water molecules. The crystalline structure forms cages that contain at most one small guest molecule. At low temperature close to freezing point of water and high pressure, these guest molecules, which are a large variety of gases or volatile liquids, can form gas hydrates when they came into contact with water under certain conditions.

Many different thermodynamic models have been suggested for predicting hydrate equilibrium conditions [1, 2], but more studies must be done.

NOMENCLATURE

a : chemical activity
A : chemical affinity
A_r : constant of proportionality
A_TV : affinity decay rate in constant temperature and volume
K : equilibrium constant
n : number of mole of gas that occupied the cavities
n_w : number of water molecules
NH : number of hydrate forming gas
N_cav : number of cavities in hydrate structure
P : pressure
Q : amount of equilibrium constant in non-equilibrium conditions
R : universal gas constant
t : time
t_k : time required to get equilibrium conditions.
T : temperature
V : volume
Z : compressibility factor

Greek letters:
μ : chemical potential

ν : stoichiometric coefficient of reaction
ζ_Q : extent of reaction based on mole
ζ_t : extent of reaction based on time

Subscripts:
A : initial condition for hydrate formation
B : final condition for hydrate formation
i : arbitrary component
j : arbitrary data point
about their formation and decomposition rate. There are many different views about the hydrate formation process. A semi-empirical model was proposed for the gas consumption rate [3,4]. Later an intrinsic kinetics model for hydrate growth, with only one adjustable parameter, was formulated [5]. Hydrate formation is also proposed by nucleation and growth processes. It is very difficult to distinguish between nucleation and growth rate since both processes occur simultaneously. Many researchers work on different models which heat and mass transfer are control mechanisms [6,7] but because of the complexity and stochastic nature of the process, a model is needed that uses initial and final conditions of the process to predict the formation rate.

In this work, the chemical affinity was used for modeling hydrate formation rate in a constant volume process. Moreover an experimental setup was set up to collect hydrate formation data.

MATERIALS AND PROCEDURES
The experiments were done in a system which consist of a reactor, a shell for heat transfer and a data acquisition system. A schematic of apparatus is shown in Fig. 1 and detail description of apparatus and procedure are given in [8].

MODELING
Chemical affinity
Chemical affinity $A$, is defined as a generalized driving force for chemical reactions as [9]:

$$A = -\sum v_i \mu_i$$  \hspace{1cm} (1)

where $\mu_i$ is the chemical potential of component $i$. According to this definition, at equilibrium $A = 0$, and in any state in which the reaction proceeds spontaneously $A > 0$.

Classically, the chemical potential $\mu_i$ of component $i$ in any arbitrary state can be related to its chemical potential $\mu_i^0$ in some standard state by an equation of the form

$$v_i \mu_i = v_i \mu_i^0 + RT \ln (a_i)^0$$  \hspace{1cm} (2)

where $R$ is the gas constant and $a_i$ is the activity of component $i$.

Equation (2) can be expressed in terms of affinity by substituting from equation (1) to yield

$$A = A^0 - RT \sum_i \ln (a_i)^0$$  \hspace{1cm} (3)

then equation (4) can be rewritten as

$$A = A^0 - RT \ln (Q)$$  \hspace{1cm} (5)

at reaction initiation $Q = 0$, so that $A = \infty$; while at equilibrium $A = 0$, so that $A^0 = RT \ln (K)$, where $K$ is the thermodynamic equilibrium constant.

Substituting for $A^0$ in equation (5) yields

$$A = -RT \ln (\zeta_Q)$$  \hspace{1cm} (6)

where $\zeta_Q = \frac{Q}{K}$. By definition, the value of $\zeta_Q$ is limited to the range $0 \leq \zeta_Q \leq 1$; and its standard state value $\zeta_Q^0$ is equal to $\frac{1}{K}$. Hence, $\zeta_Q$ is a dimensionless measure of the extent of reaction from $A = \infty$ to $A = 0$.

Accordingly, for any chemical reaction proceeding spontaneously in a closed system of fixed volume $V$ and at constant temperature $T$, the affinity decays towards zero, so that

$$\dot{A}_{T,V} < 0$$  \hspace{1cm} (7)

where $\dot{A}_{T,V} = \left( \frac{\partial A}{\partial t} \right)_{T,V}$ is the affinity decay rate.

The calculated values of $\dot{A}_{T,V}$ were correlated with various functions of elapsed time $t_i$ by a regression analysis to determine the best data fit. However as soon as the reciprocal-time relationship was examined it was apparent that...
\( \dot{A}_{T,Y} \) was inversely proportional to the elapsed time [10]
\[
\dot{A}_{T,Y} \propto \frac{1}{t} + I
\] (8)

Because of \( \dot{A}_{T,Y} = 0 \) at the equilibrium (or end of reaction), the intercept (I) must depend on the time of achieving the equilibrium (\( t_K \)) and it can rearrange the Eq. (8) to:
\[
\dot{A}_{T,Y} = A_r \left[ \frac{1}{t} - \frac{1}{t_K} \right]
\] (9)
where \( A_r \) is a constant of proportionality, and denotes the affinity rate constant.

In order to directly correlate the calculated values of the chemical affinity with the measured values of the elapsed time Eq. (9) must be integrated, which yields
\[
A_i = A_r \ln[\xi_{t_i} \cdot \exp(1 - \xi_{t_i})]
\] (10)
where \( \xi_{t_i} = \left( \frac{t_i}{t_K} \right) \) is similar to \( \zeta_Q \), and the extent of reaction \( \xi_{t_i} \) is limited to the range \( 0 \leq \xi_{t_i} \leq 1 \).
However the value of \( \xi_{t_i} \) must be known to correlate empirical data by Eq. (11) so as to determine the value of \( t_K \), but \( \xi_{t_i} \) itself depends on \( t_K \). This obstacle was overcome by generating values of \( t_K \) by an iterative subroutine [11].

Hydrate formation modeling
As shown in Fig.2 the experimental conditions for hydrate formation must be far away from the 3-phase equilibrium curve (like point A). In a constant volume – constant temperature experiments after the formation of hydrate crystals; pressure decreases gradually because of gas consumption and the final pressure must be equal to \( P_{eq} \) (point B). At this point, hydrate formation stops and the system reaches equilibrium.

In this research, the main assumption is that there is similarity between hydrate formation and chemical reaction in constant T and V conditions. Both processes progress until they reach equilibrium conditions. Then we supposed that hydrate formation is a chemical reaction similar to the following [12]:
\[
\sum_{i=1}^{NH} \left( \frac{n_i}{N_{cav}} \right) g_i + n_w H_2O \rightarrow \left[ \sum_{i=1}^{NH} \frac{n_i}{N_{cav}} g_i n_w H_2O \right]
\] (11)
where \( n_i/N_{cav} \), \( n_w \) are stoichiometric coefficients of reaction for hydrate formation gas and water respectively.

For calculating of affinity in different conditions we must measure the extent of reaction with time by using the pressure of gas in each elapsed time. As shown in Fig. 2, the amount of total gas consumed during hydrate formation is equal to \( (n_A - n_B) \) and the extent of reaction can be obtain from
\[
\zeta_Q = \frac{n_A - n}{n_A - n_B} = \frac{(P_A/Z_A) - (P_l/Z)}{(P_A/Z_A) - (P_l/Z_B)}
\] (14)
and we obtain affinity for each time by the formula
\[
A_i = -RT \ln(\zeta_Q)
\] (15)
By plotting \( A_i \) versus \( \ln[\xi_{t_i} \cdot \exp(1 - \xi_{t_i})] \), we can obtain \( A_r \) \( t_K \).

Figure 2  Hydrate formation condition in constant temperature

RESULTS AND DISCUSSION

\[ n = \frac{PV}{ZRT} \] (13)

Now, the Eq. (12) can be rewritten as
\[
\zeta_Q = \frac{n_A - n}{n_A - n_B} = \frac{(P_A/Z_A) - (P_l/Z)}{(P_A/Z_A) - (P_l/Z_B)}
\] (14)
and we obtain affinity for each time by the formula
\[
A_i = -RT \ln(\zeta_Q)
\] (15)

Hydrate 3 phase Equilibrium Curve
The results at different temperatures and at initial experimental pressure are shown in Figs. 3-7 for methane and Figs. 8-10 for propane (because of simplicity the letter q was shown for $\zeta$ in these figures). Compressibility of gas phase was calculated by PR equation of state.

As we have seen there is a linear relation between data. The experiments were done for methane at temperatures 274, 276, 278, 280, 282 K and for propane at temperatures 274, 275, 276 K with different initial pressures. The calculated $A_r$, $t_K$ are given in Table 1 for methane and Table 2 for propane.

Figure 3 Affinity versus $\ln[\zeta_i \exp(1 - \zeta_i)]$ for methane at 274 K and different initial pressures.

Figure 4 Affinity versus $\ln[\zeta_i \exp(1 - \zeta_i)]$ for methane at 276 K and different initial pressures.

Figure 5 Affinity versus $\ln[\zeta_i \exp(1 - \zeta_i)]$ for methane at 278 K and different initial pressures.

Figure 6 Affinity versus $\ln[\zeta_i \exp(1 - \zeta_i)]$ for methane at 280 K and different initial pressures.

Figure 7 Affinity versus $\ln[\zeta_i \exp(1 - \zeta_i)]$ for methane at 282 K and different initial pressures.

Figure 8 Affinity versus $\ln[\zeta_i \exp(1 - \zeta_i)]$ for propane at 274 K and different initial pressures.

Figure 9 Affinity versus $\ln[\zeta_i \exp(1 - \zeta_i)]$ for propane at 275 K and different initial pressures.
Figure 10: Affinity versus $\ln[\zeta_i \exp(l - \zeta_i)]$ for propane at 276 K and initial pressure.

The variation of the reactor pressures with time was calculated using averaged $A_r$, $t_k$ for each temperature from results in Table 1 and Table 2 for the experiments. In these experiments, the variation of the pressures in the hydrate formation reactor with time was measured and shown in Figures 11(a to q) for methane and 12(a to h). Figs. 11 and 12 demonstrate that there is a good agreement between calculated results and experimental data at low pressure near the 3-phase equilibrium curve in most experiments. However for the high pressure experiments, such agreements exist at the beginning of the experiments. It can be observed from high pressure experiments that the final pressure of the reactor is not $P_{eq}$ (point B in Fig. 2). Theoretically, the final pressure must be equal to the pressure of point B. We know if the conditions of hydrate formation were far from equilibrium (high driving force or high initial pressure) the nuclei from crystallization would become very small and the rate of hydrate formation would be high, then a large amount of hydrates would form in a short time. If the mixing of the reactor were not sufficient (in our experiments mixing is prepared by movement of mercury in the reactor), hydrates would aggregate in the gas-liquid inter-phase and reduce the mass transfer area and the kinetics of hydrate formation would be affected by mass transfer of gas into liquid. These are the mainsprings of the differences between experimental and modeling results at high initial pressures and if there was a good mixing within the reactor, the agreement of model will be good. We ignored the last data of experiments that don’t get the $P_{eq}$ in each experiments and calculation of $A_r$ and $t_k$ was based on the first rate data. Also this model can be applied for crystals I and II gases.

### Table 1. Calculated parameters of model for methane at different conditions

<table>
<thead>
<tr>
<th>$T_{exp}$ (K)</th>
<th>$P_{initial}$ (Bar)</th>
<th>$A_r$ (J/mol)</th>
<th>$t_k$ (Sec)</th>
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### Table 2. Calculated parameters of model for propane at different conditions

<table>
<thead>
<tr>
<th>$T_{exp}$ (K)</th>
<th>$P_{initial}$ (Bar)</th>
<th>$A_r$ (J/mol)</th>
<th>$t_k$ (Sec)</th>
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Figure 11.a Calculated and experimental rate data for methane (T=274 K and Pinitial=45.13 bar)

Figure 11.c Calculated and experimental rate data for methane (T=274 K and Pinitial=69.16 bar)

Figure 11.e Calculated and experimental rate data for methane (T=276 K and Pinitial=55.11 bar)

Figure 11.g Calculated and experimental rate data for methane (T=276 K and Pinitial=79.25 bar)

Figure 11.j Calculated and experimental rate data for methane (T=278 K and Pinitial=71.63 bar)

Figure 11.l Calculated and experimental rate data for methane (T=278 K and Pinitial=87.96 bar)
Figure 11.n Calculated and experimental rate data for methane (T=280 K and P_initial =81.36 bar)

Figure 11.o Calculated and experimental rate data for methane (T=280 K and P_initial =88.84 bar)

Figure 11.q Calculated and experimental rate data for methane (T=282 K and P_initial =90.68 bar)

Figure 12.b Calculated and experimental rate data for propane (T=274 K and P_initial =3.38 bar)

Figure 12c Calculated and experimental rate data for propane (T=274 K and P_initial =4.0 bar)

Figure 12.f Calculated and experimental rate data for propane (T=275 K and P_initial =4.08 bar)
CONCLUSIONS
There are many models in literature for gas hydrate formation that using a microscopic driving force like mass transfer from gas phase to water or heat transfer between solid particles and the bulk of liquid. Such models need experimental parameters like the mass transfer coefficients or heat transfer coefficients or population of particles and these coefficients differ for each experiment. But in this research a conceptual model was proposed that define a macroscopic driving force that only need the initial condition (experimental condition, temperature and pressure) and final conditions (equilibrium conditions). The basic idea is that there is a unique path for each experiment which the crystallization process decays the affinity. Microscopic phenomena such as mass transfer, heat transfer, nucleation occurs in their special rates and causes the overall formation rate so that the time for this affinity decay is minimal. Because of the thermodynamic relation between affinity and Helmholtz free energy, this model can directly and easily be used for gas mixture and predicting the $A_r$ for pure gases.

REFERENCES