

# Modeling of Methane Hydrate Decomposition by Using Chemical Affinity

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**ABSTRACT:** In this work, experimental kinetics data of methane hydrate decomposition at temperatures ranging from 272.15 to 276.15 K and at pressures ranging from 10 to 30 bars were modeled by using chemical affinity. This model proposed a macroscopic model which is independent of any intermediate mechanism like heat or mass transfer. The results show there is good agreement with experimental data. Also the two parameters of model were calculated and correlation coefficient of model is higher than 0.9.

**KEY WORDS:** Affinity, Methane, Decomposition kinetics, Gas hydrate.

## INTRODUCTION

Gas hydrate is a solid solution which is formed from mixing of light hydrocarbon gases or light non-hydrocarbon gases with water at temperature that is close to freezing point of water and high pressures.

One of the problems encountered in petroleum industry is hydrate plugging in the gas transportation pipeline. So having reliable data on the kinetics of gas hydrate decomposition could allow for better predictions of the rate of decomposition in hydrate plugs. On the other hand, existence of huge hydrate reservoirs in permafrost regions and under the ocean floor as important sources of energy for future increases the importance of hydrate decomposition and prediction of production rate of gas from these reservoirs. The kinetics of hydrate formation was first measured by Vysniauskus & Bishnoi [1]. Englezos, Dholabhai, Kalogerakis & Bishnoi recognized that the hydrate formation was a crystallization process [2] while the kinetics of hydrate formation has been studied

in a few systems, relatively little attention has been paid to gas hydrate decomposition. Ullrich, Selim & Sloan described the decomposition of a synthetic core of methane hydrate as a moving boundary heat transfer problem [3]. Kim, Bishnoi, Heidmann & Rizvi developed a model for the intrinsic rate of gas hydrate decomposition and determined the rate constant from experimental data for methane [4]. Kamath studied the process of hydrate dissociation by heating [5]. The kinetics of gas hydrate decomposition has been studied by Clarke & Bishnoi [6, 7]. They determined the intrinsic rate of ethane hydrate decomposition and methane hydrate decomposition. All of the models noted above, used the microscopic mechanisms like heat or mass transfer but in this work, a model is discussed for methane hydrate decomposition by chemical affinity, which is independent of microscopic mechanisms but depends only on initial and final condition of experiments.

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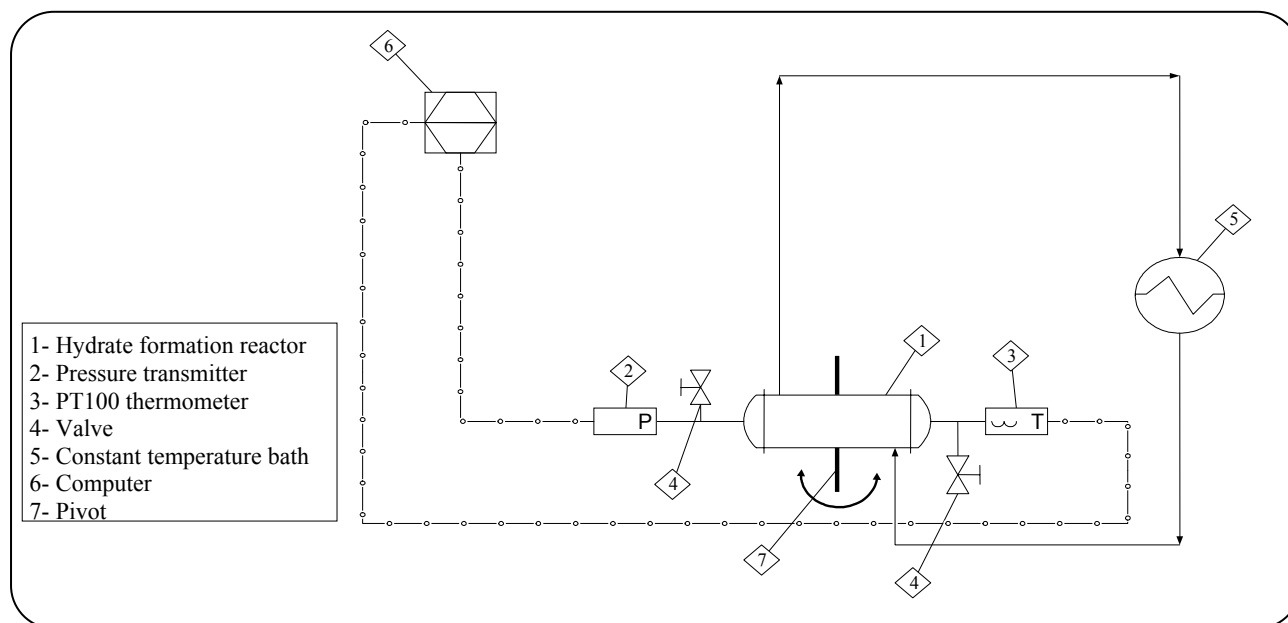


Fig. 1: Experimental setup, Hydrate Decomposition apparatus [8].

## EXPERIMENTAL APPARATUS AND PROCEDURE

The experiments were done at a high pressure vessel which consist of a shell for heat transfer and a data acquisition system [8]. The apparatus is shown in Fig. 1. Hydrate formation reactor was made by a 0.75 inch Schedule No. 80, stainless steel 316 pipe. At the two ends of these pipes a pressure transmitter and a thermometer was installed. The volume of reactor was 120 CC. The pressure of reactor was measured using a Druck PTX1400 pressure transmitter (0–10MPa) with accuracy of about  $\pm 0.25\%$  of the scale (i.e. 25 kPa) and the temperature of reactor was measured using PT100 thermometers with an accuracy of  $\pm 0.1$  K. The measured values can be recorded by a data acquisition system driven by a personal computer. The temperature of the reactor is controlled by the flow of an ethanol-water solution by an external circulating temperature bath through the shell. A Lauda RE 210 temperature bath was used to control the temperature of the cooling fluid. The reactor is mounted on a pivot and mixing is obtained by rocking the vessel. The methane having a high (nominal) purity of 99.999% supplied by Air products was used. The distilled water was also used. The hydrate formation reactor was firstly evacuated. Then 30 cc of mercury (for enhancing the mixing) and 40 cc of distilled water were charged to the reactor. The reactor was then pressurized to a pressure of about 0.05 MPa below the equilibrium

pressure for the hydrate formation at the specified experimental temperature. The constant temperature bath was turned on and the reactor was allowed to reach the constant experimental temperature. When the solution attained thermal equilibrium, the reactor was pressurized to the experimental pressure by injection of gas from the cylinder, and mixing was started and now data collection starts. After hydrate formation and reaching the equilibrium pressure, suddenly the pressure of system decreased by releasing of gas to a pressure below the 3 phase equilibrium and the decomposition began. Then we could start data collection for modeling.

## MODELING

### Chemical affinity

The driving force for reaction is the chemical potential difference between the products and the reactants, and the reaction is completed to reduce this difference. At first the chemical affinity that is shown by "A", was defined as a thermodynamic function by *De Donder* [9]. All chemical reactions followed the direction that decreases the chemical affinity. *Prigogine* defined the chemical affinity as generalized driving force for chemical reaction and explained it as follows [10]:

$$A = -\sum \nu_i \mu_i \quad (1)$$

Where  $\mu_i$  is chemical potential and  $\nu_i$  is the stoichiometric coefficient of  $i$ th compounds. Also, at equilibrium state  $A=0$  and at the other state ( $A>0$ ) that reaction is advancing toward equilibrium. We can write chemical affinity as follow [11]:

$$A = -RT \ln \zeta_Q \quad (2)$$

Where  $\zeta_Q = Q/K$  is limited to the range  $0 \leq \zeta_Q \leq 1$ . It is the extent of reaction from  $A=\infty$  to  $A=0$ .

Thus for each reaction that is occurring in a closed, isochor and isotherm system, Affinity limits towards zero so  $A_{T,V} = [\partial A / \partial t]_{T,V} < 0$ . The best function that predicts decreasing of chemical affinity was introduced as [12]:

$$A_{T,V} = A_r \left[ \frac{1}{t} - \frac{1}{t_K} \right] \quad (3)$$

Where  $A_r$  is a constant denoting the affinity rate constant and  $t_K$  is time of achieving equilibrium. Because this equation describes decaying of affinity in a reaction path independent of mechanism of reaction, this equation is named as natural path by *Garfinkle* [11].

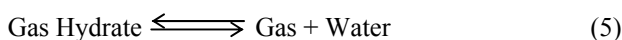
In order to relate calculated quantities of chemical affinity with time, we must integrate Eq. (3), so follows

$$A_i = A_r \cdot \ln[\zeta_{t_i} \cdot \exp(1 - \zeta_{t_i})] \quad (4)$$

Where  $\zeta_{t_i} = t_i/t_K$  is similar to  $\zeta_Q$ , the extent of reaction  $\zeta_{t_i}$  is limited to the range  $0 \leq \zeta_{t_i} \leq 1$ . On the other hand, the value of  $\zeta_{t_i}$  must be known to correlate empirical data with time, but  $\zeta_{t_i}$  itself depends on  $t_K$ . This problem can be solved by generating values of  $t_K$  by an iterative method.

### Hydrate decomposition modeling

This method of modeling was used for formation of gas hydrate successfully by *Izadpanah et al.* [12]. If we supposed that hydrate decomposition is as a chemical reaction like the following:



As shown in Fig. 2 for hydrate decomposition the experimental conditions must be far away from the 3-phase equilibrium curve (like point A). In a constant volume-constant temperature experiments after the decomposition of hydrate crystals; pressure increases

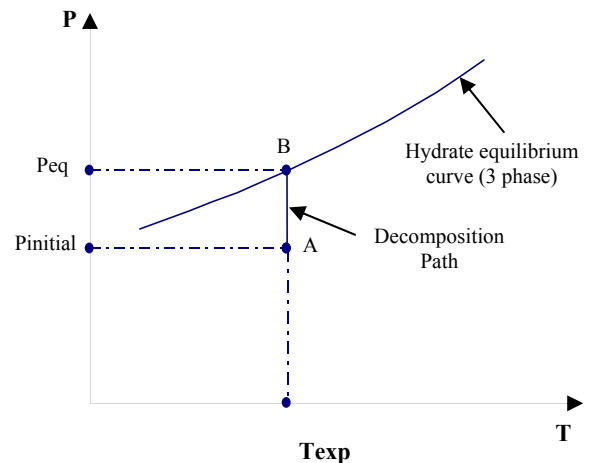


Fig. 2: Hydrate decomposition condition in constant temperature.

gradually because of gas production and the final pressure must be equal to  $P_{eq}$  (point B). At this point, the hydrate decomposition stops and system reaches equilibrium.

For calculating the affinity, we must measure the extent of reaction with time by using experimental pressure-time data of gas production. As shown in Fig. 2 the amount of total gas produced during hydrate decomposition is equal to  $(n_B - n_A)$  and the extent of reaction can be obtained from:

$$\zeta_{Qi} = \frac{n_i - n_A}{n_B - n_A} \quad (6)$$

For calculating the number of mole of gas by using measured pressure at system condition we can use an equation of state to calculate the compressibility of gas phase and then calculate the number of moles of gas as

$$n = \frac{PV}{ZRT} \quad (7)$$

Then the Eq. (6) can be rewritten as

$$\zeta_{Qi} = \frac{n_i - n_A}{n_A - n_B} = \frac{(P_i/Z_i) - (P_A/Z_A)}{(P_B/Z_B) - (P_A/Z_i)} \quad (8)$$

And we obtain affinity in each time by this formula

$$A_i = -RT \ln(\zeta_{Qi}) \quad (9)$$

By plotting  $A_i$  versus  $\ln[\zeta_{t_i} \cdot \exp(1 - \zeta_{t_i})]$  we can obtain  $A_r$ ,  $t_K$  by iteration methods [12].

## RESULTS AND DISCUSSION

In this research, the experimental kinetics data of methane hydrate decomposition at four temperatures 272.15 to 276.15 K and at pressures ranging from 10 to 30 bars were modeled. Some of the results are shown in Fig. 3-10 in different temperatures and at initial experimental pressures. As we have seen there is a linear relation between data. The calculated  $A_r$ ,  $t_k$  are given in Table 1. By considering the results in Fig. 3-10, we found that there is a good agreement between calculated results and experimental data because all correlation coefficients ( $r^2$ ) are higher than 0.9. Also at the start of decomposition process the model has no good agreement because of decomposition process is an endothermic process and decreasing the pressure of reactor to the below of 3-phase equilibrium curve caused the decreasing of temperature and the constant temperature assumption of all process is incorrect until the bath can control the temperature. Also the final pressure of all of the experiments that occurred in  $T_{exp}$  must be equal to  $P_{eq}$ , but because of difficulty of temperature setting at initial time of experiments this value differed among diffluent experiments.

## CONCLUSIONS

There are few models in literatures for gas hydrate decomposition kinetics using microscopic driving force like mass transfer or heat transfer between solid particles and bulk of liquid, these models need parameters like mass transfer coefficients or heat transfer coefficients that differ at each experiment. Also determination of these parameters is difficult and there are no accurate experiments or correlations to measure or calculate them. This model do not need to any distribution function of particles like usual crystallization model. In this research a conceptual model was proposed that defines a macroscopic driving force and uses only the initial conditions (temperature and pressure) and final conditions (equilibrium conditions). The basic idea is that there is only a unique path for each experiment that on this path the decomposition process decays the affinity.

## Nomenclature

$a$	Chemical activity
$A$	Chemical affinity
$A_r$	Affinity rate constant
$\dot{A}_{T,V}$	Affinity decay rate in constant temperature and volume

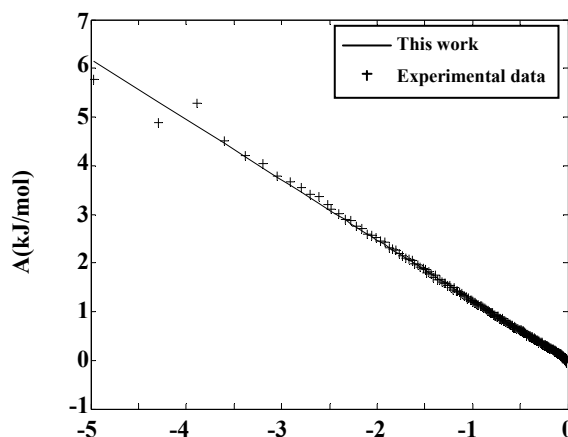


Fig. 3: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1-\zeta_{t_i})]$  for methane hydrates decomposition.  $T=272.15$  K,  $P_{initial}=15.3$  bar.

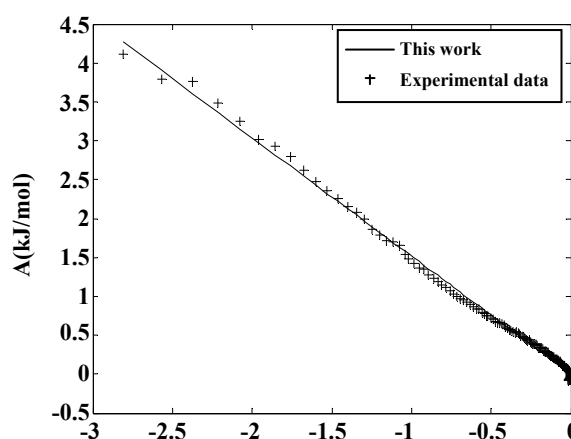


Fig. 4: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1-\zeta_{t_i})]$  for methane hydrates decomposition.  $T=272.15$  K,  $P_{initial}=18.1$  bar.

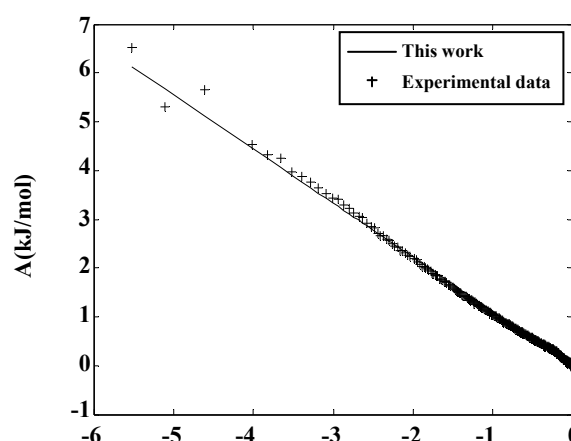


Fig. 4: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1-\zeta_{t_i})]$  for methane hydrates decomposition.  $T=273.15$  K,  $P_{initial}=20$  bar.

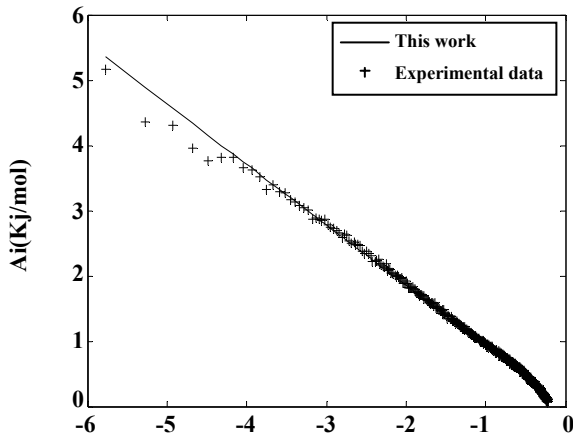


Fig. 6: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1-\zeta_{t_i})]$  for methane hydrates decomposition.  $T=273.15$  K,  $P_{initial}=23.5$  bar.

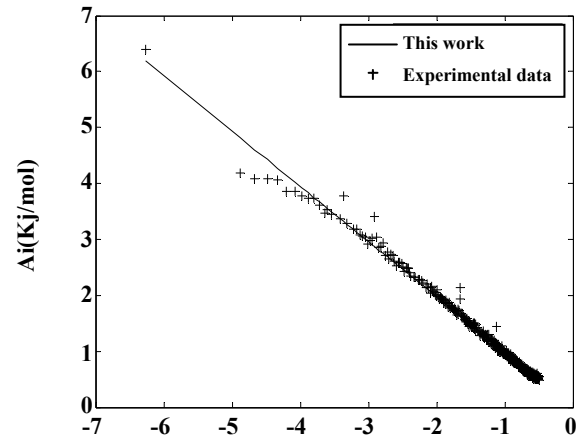


Fig. 8: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1-\zeta_{t_i})]$  for methane hydrates decomposition.  $T=274.15$  K,  $P_{initial}=24.8$  bar.

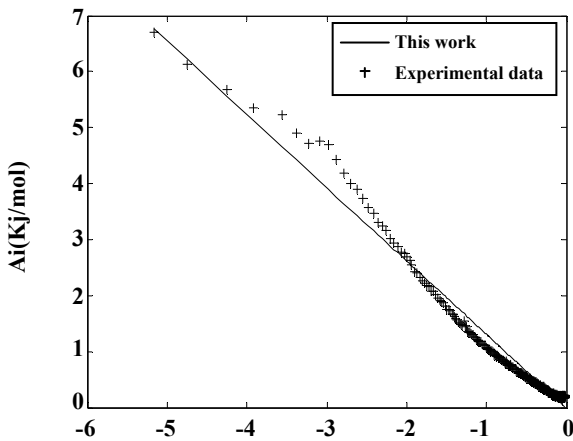


Fig. 7: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1-\zeta_{t_i})]$  for methane hydrates decomposition.  $T=274.15$  K,  $P_{initial}=20.6$  bar.

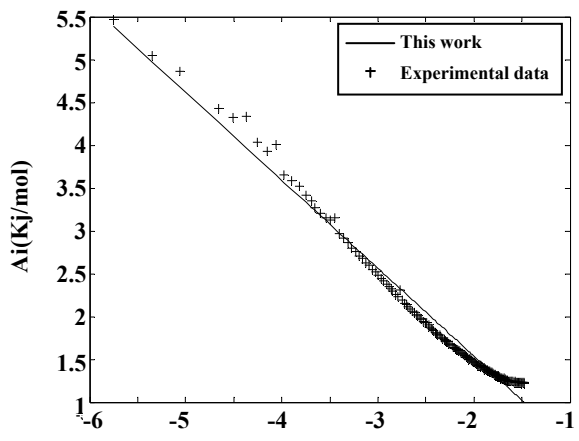


Fig. 9: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1-\zeta_{t_i})]$  for methane hydrates decomposition.  $T=275.15$  K,  $P_{initial}=14.7$  bar.

K	Equilibrium constant
n	Number of mole of gas
P	Pressure
Q	Equilibrium constant in non-equilibrium conditions
R	Universal gas constant
t	Time
$t_k$	Time required getting equilibrium conditions
T	Temperature
V	Volume
Z	Compressibility factor

#### Greek letters

$\mu$	Chemical potential
$\zeta_Q$	Extent of reaction based on mole

$\nu_i$	Stoichiometric coefficient of reaction of component i
$\zeta_i$	Extent of reaction based on time

#### Subscripts

A	Initial condition for hydrate decomposition
B	Final condition for hydrate decomposition
i	Arbitrary component

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Table 1: Calculated parameters of model.

$T_{\text{exp}}$ (K)	$P_{\text{initial}}$ (bar)	$P_{\text{final}}$ (bar)	$t_{\text{K}}$ (S)	$A_r$ (kJ/mol)	$r^2$
272.15	18.1	25.8	310	-1.51	0.99
	21.8	25.6	297	-0.75	0.98
	20.4	25.4	919	-1.12	0.99
	15.3	25.2	786	-1.24	0.99
273.15	12.2	28.7	2095	-3.06	0.97
	16.7	28.5	1123	-1.10	0.98
	23.5	28.5	2634	-0.93	0.99
	20.0	28.3	1354	-1.11	0.99
274.15	25.0	31.5	969	-1.25	0.92
	20.4	30.7	1024	-1.07	0.97
	24.8	30.0	2866	-0.98	0.99
	20.6	31.2	945	-1.31	0.97
	18.1	31.3	1580	-1.09	0.98
275.15	26.3	34.1	541	-1.77	0.98
	15.6	34.0	1931	-1.11	0.96
	11.1	33.8	3000	-0.47	0.99
	15.5	34.7	1918	-1.02	0.98
	14.7	33.9	2993	-0.42	0.97
276.15	30.3	37.4	2824	-0.62	0.99
	16.5	37.4	1363	-0.73	0.99
	23.8	37.3	822	-1.02	0.98
	20.8	37.2	1467	-1.30	0.98
	25.6	37.0	2321	-1.05	0.99

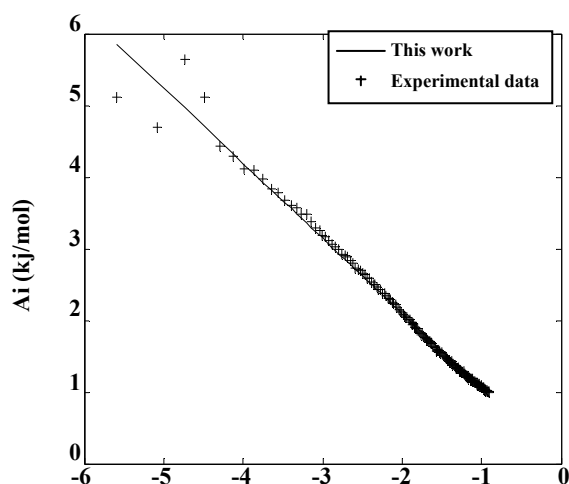


Fig. 10: Affinity versus  $\ln[\zeta_{t_i} \cdot \exp(1 - \zeta_{t_i})]$  for methane hydrates decomposition.  $T=276.15$  K,  $P_{\text{initial}}=25.6$  bar.

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