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Formation and dissociation reaction rates and relevant kinetic behavior of propane gas hydrate (PGH)

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**Formation and Dissociation Reaction Rates and Relevant Kinetic Behavior
of Propane Gas Hydrate (PGH)**

by

Feng Song

**Thesis Submitted to the College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

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**Morgantown, West Virginia
2001**

Keywords: propane gas hydrate, sediments, kinetics, formation, dissociation

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ABSTRACT

Formation and Dissociation Reaction Rates and Relevant Kinetic Behavior of Propane Gas Hydrate (PGH)

Feng Song

The formation and dissociation reaction rates and their kinetic behavior of propane gas hydrate (PGH) within the well-defined sediment particle's packing structures were experimentally investigated in this work by using a multi-phase heterogeneous reaction system, consisting of propane gas (g), water (l), PGH (s) and sediment particles (glass beads) (s). This work was carried out under the formation conditions of $P=0.427$ MPa and $T=273.5$ K, and under the dissociation conditions of $P\leq 0.168$ MPa and $T=273.5$ K.

A new designed, isothermal, and packed bed batch reactor was used for the kinetic analysis of the above defined PGH reaction system under the smooth operating conditions, yielding the satisfactory, reproducible material balance. Quantitative overall reaction rates of PGH formation and dissociation were derived and orders of the above reactions were experimentally obtained.

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NOTATION

D_p :	Diameter of sediment's particles [μm]
g :	Gas
k_d :	Dissociation reaction rate constant [$\text{lit}^{-1} \text{hr}^{-1}$]
k'_d :	Dissociation reaction rate constant [hr^{-1}]
k_f :	Formation reaction rate constant [$\text{lit}^{-1} \text{hr}^{-1}$]
k'_f :	Formation reaction rate constant [hr^{-1}]
l :	Liquid
N_g :	Mole amount of propane gas left in the reactor [mole]
n_0 :	Mole amount of propane gas fed into the reactor at time=0 [mole]
n_g :	Mole amount of propane gas in the reactor defined in equation (11) [mole]
n_H :	Mole amount of PGH formed at time t [mole]
$n_{\text{H}_2\text{O}}$:	Mole amount of water fed into the reactor at the beginning [mole]
n^* :	Overall formation reaction order [-]
n'_0 :	Mole amount of PGH in the reactor at time=0 [mole]
n'_H :	Mole amount of PGH left in the reactor at time t [mole]
n'_g :	Mole amount of propane gas generated at time t [mole]
$n^\#$:	Overall dissociation reaction order [-]
P :	Pressure of the gas receiver [MPa]
$P(t)$:	Pressure of the reactor at time t [MPa]

PGH:	Propane gas hydrate
P_{eq} :	Equilibrium pressure [MPa]
S:	Water saturation degree in porous sediments [%]
s:	Solid
T:	Temperature of the reactor [K]
T_{room} :	Temperature of the gas receiver [K]
t:	Reaction time [hr]
$V_{C_3H_8}$:	Volume of propane gas generated from PGH [lit]
$V_{gs \text{ in PB}}$:	Volume of the gas space in the packed bed [lit]
V_{H_2O} :	Volume of water in porous sediments at the beginning [lit]
$V_{I \text{ gs}}$:	Volume of gas space [lit]
V_{PB} :	Volume of the packed bed (cage) [lit]
V_R :	Volume of the reactor [lit]
V_s :	Volume of particles (sediments) [lit]
$V_{T \text{ gs}}$:	Total volume of the gas space in the reactor [lit]
V_{ε} :	Volume of void in porous sediments [lit]
$v(t)$:	Specific volume of propane gas in the reactor at time t[lit/mole]
z:	Compressibility factor [-]

Greek

ε :	Porosity of dry sediments [-]
-----------------	-------------------------------

Subscribe

0: At time=0

d: Dissociation

eq: Equilibrium

f: Formation

g: Gas

gs: Gas space

gs in PB: Gas space in packed bed

H: Hydrate

PB: Packed bed

p: particles

R: Reactor

T gs: Total gas space

CHAPTER 1 INTRODUCTION

1.1 Objectives of This Work

The resources of natural gas hydrates (NGH) (such as methane gas hydrate (MGH), ethane gas hydrate (EGH), and propane gas hydrate (PGH)) have recently been found to be one of the most important energy resources in this new century. The formation and dissociation reaction rates and their kinetic behavior of propane gas hydrate (PGH) within the well-defined sediment particle's packing structures were experimentally investigated in this work by using a multi-phase heterogeneous reaction system, consisting of propane gas (g), water (l), PGH (s) and sediment particles (glass beads) (s).

In the past open literature there have been almost no systematic experimental data of NGH, particularly PGH formation and dissociation rates published for the above reacting system.

The PGH formation reactions in our work were carried out under the conditions of $P=0.427$ MPa and $T=273.5$ K, and the dissociation reaction under the conditions of $P\leq 0.168$ MPa and $T=273.5$ K.

A custom designed, isothermal, and packed bed batch reactor was used for the kinetic analysis of the above defined PGH reaction system under the smooth operating conditions, yielding the satisfactory, reproducible material balance.

Quantitative overall reaction rates of PGH formation and dissociation were derived and the orders of the above reactions were experimentally obtained. The effects of the major parameters, such as the primary sediment particle size, porosity, and water saturation

degree on the reaction mechanisms were obtained experimentally. The dissociation rates in this study were measured by depressurization method.

1.2 Background

1.2.1 General Description of Natural Gas Hydrates and Their Structures

Natural Gas Hydrates (NGH) are clathrate crystal compounds in which water molecules (host molecules) form cage-like structures around smaller guest molecules. NGH generally consists of the water (host) and smaller gas molecules (guest), which are such as methane gas, ethane gas, propane gas, butane gas etc. There are three structures of NGH: structure I (sI), structure II (sII), and structure H (sH). Each has different number of water and gas molecules. The ratio of water molecules to gas moles is called “hydration number”.

Structure I hydrate contains 46 water molecules per 8 gas molecules. The hydration number is 5.75. The water molecules form 2 small dodecahedral voids (diameter: 5.02×10^{-1} nm) and 6 large tetradecahedral voids (diameter: 5.87×10^{-1} nm). These voids can only be occupied by small gas molecules (such as methane diameter: 4.36×10^{-1} nm, and ethane diameter: 5.50×10^{-1} nm) with molecular diameter not exceeding 5.2×10^{-1} nm.

Structure II hydrate contains 136 water molecules per 24 gas molecules. The hydration number is 5.67. The water molecules form 16 small dodecahedral voids (diameter: 5.02×10^{-1} nm) and 8 large hexakaidecahedral voids (diameter: 6.66×10^{-1} nm). They may contain gases with molecular dimensions from 5.9×10^{-1} nm to 6.9×10^{-4} nm, such as propane, and butane. Propane molecules can only occupy the large voids (hexakaidecahedral voids) of structure II due to the larger molecules (diameter: 6.28×10^{-1} nm).

Figure 1 and **Figure 2** show the unit cell of structure II and relative sizes of hydrate guests and host cavities respectively.

One dodecahedron consists of 12 pentagonal planes, and one hexakaidecahedron consists of 12 pentagonal planes and 4 hexagonal planes in **Figure 1**.

Further detailed general description of the characteristics of NGH could be obtained from several literatures of Sloan (1998) and Makogon (1997).

Figure 1 Unit cell of a gas hydrate structure II (Fleyfel 1993)
 (Consisting of 16 of 5^{12} and 8 of $5^{12}6^4$)

Figure 2 Relative sizes of hydrate guests and host cavities (Sloan 1998)

1.2.2 Natural Gas Hydrates as a Future Energy Resource

From the density of methane gas hydrate (900 kg/m^3) and the hydration number of methane gas hydrate (5.75), it is easily to obtain that 1 m^3 of methane gas hydrate can generate about $7.53 \times 10^3 \text{ m}^3$ of methane gas.

Since the Russian discovered in-situ reserves of gas hydrates in the late 1960's, gas hydrates have been considered as a potential natural gas resource used in the future.

Today, most of geologist scientists estimate it on the low side, approximately 100,000 trillio cubic feet (TCF), and on the high side, 270,000,000 TCF (Collett et al. 1998). The US currently uses about 20 TCF of natural gas per year, so it is very obvious to know that natural gas hydrates are really huge energy resources for the whole world, if all natural gas hydrates could be recoverable.

In USA, natural gas hydrate deposits have been confirmed on all area of the continental shelf and under Alaskan permafrost. Similar deposits have been confirmed in many locations throughout the world. Makogon (1997) provided more detailed information of the hydrate deposits around the world. Thus, the resources of natural gas hydrates (NGH) have now been recognized as one of the most significant energy material for twenty-first century.

1.2.3 Kinetics of Hydrate Formation

Hydrate formation usually involves the nucleation and growth of the hydrates. Hydrate nucleation is the process, during which small hydrate crystals (nuclei) grow and disperse in an attempt to achieve critical size for continued growth. Current hypothesis for hydrate

nucleation are based on the better-known phenomena of water freezing, the dissolution of hydrocarbons in water, and computer simulations of both phenomena.

Hydrate formation usually occurs at the vapor-liquid interface, not only because the interface lowers the Gibbs free energy of nucleation, but also because the interface is the location of the required very high concentrations of the host and guest molecules.

Due to the large amount of gas in hydrates relative to that dissolved in the liquid, the most likely place for the crystals to nucleate and grow is at the vapor-water interface with the high concentrations of each constituent. The hydrate structure at the interface provides an organizing template for combination of the large amounts of gas and liquid. High mixing rates may cause interfacial gas + liquid + crystal structures to be dispersed within the liquid, giving the appearance of bulk nucleation from a surface effect.

Sloan (1998) proposed a cluster nucleation model (shown in **Figure 3**) with the following elements:

1. Pure water exists without guests, but with many transient, labile ring structures of pentamers and hexamers.
2. Water molecules form labile clusters around dissolved guest's molecules.
3. Clusters of dissolved species combined to form unit cells
4. An activation barrier is associated with the cluster transformation.

Hammereschmidt (1934) first indicated that there could be an induction period associated with the appearance of the first crystals from a hydrocarbon-water mixture, which has a suitable composition, and its pressure and temperature are such that, thermodynamically, hydrates could form.

Figure 3 Schematic Model of Hydrate Cluster Growth (Sloan 1998)

Graauw and Rutten (1970) proposed a mass-transfer-based model for the kinetics of hydrate formation. They used chloride and propane as the hydrate-formation substances. Their results showed that mass transfer at the hydrate-forming substance-water interface could be a rate-determining factor. They also found that the presence of electrolytes did not have any effect.

Makgon (1981) cited work that had been carried out in Russia. He examined the morphology of hydrate crystals and described the factors, which affect hydrate nucleation and growth. Supercooling, pressure, temperature, state of water, composition, and state of gas hydrate-forming system were mentioned as factors that affect the growth. He highlighted the importance of the knowledge of the properties of water in understanding nucleation and growth.

Vysnauskas and Bishnoi (1983) reported the first experimental results on methane hydrate formation. They also presented an empirical model that correlated the rate with the degree of supercooling, temperature, pressure, and interfacial area. A molecular mechanism was proposed. Nucleation studies were also conducted and revealed the impact of the state of water on the induction period. These parameters were also found to influence ethane hydrate formation (Vysnauskas and Bishnoi, 1985).

The experimental setup of Vysnauskas and Bishnoi was later modified to achieve homogeneous nucleation conditions and better reproducibility. The kinetic studies on methane and ethane gas hydrate formation were repeated in that improved apparatus. The data were used for the development of a mechanistic model with one adjustable parameter per hydrate former (Englezos et al. 1987a). The model was based on the

homogeneous crystallization theory and described the kinetics of hydrate crystal growth. The nuclei were assumed to form instantaneously by primary nucleation. The difference in the fugacity of the dissolved gas and the three-phase equilibrium fugacity at the experimental temperature was defined as a driving force for hydrate crystal particle growth. The study revealed that formation of hydrates is not restricted to a thin layer close to the gas-liquid interface, but could also occur throughout the liquid phase. The model was extended to the formation of hydrates from methane and ethane mixtures of various compositions (Englezos et al. 1987b).

Skovborg et al. (1993) reported isothermal experimental data on induction times for the formation of methane and ethane hydrates. They found the induction time to be strongly dependent on the stirring rate and the magnitude of the driving force. The driving force was expressed as the difference in the chemical potential of water in the hydrate phase and water in the water phase at the system temperature and pressure.

Bishnoi et al. (1996) viewed that hydrate formation is a crystallization process that includes the nucleation and growth processes. Hydrate nucleation is an intrinsically stochastic process that involves the formation and growth of gas-water clusters to critical sized, stable hydrate nuclei. Hydrate growth process involves the growth of stable hydrate nuclei as a solid hydrate.

1.2.4 Kinetics of Hydrate Dissociation

Kamath et al. (1984) reported the results of an experimental study on the thermal dissociation of propane gas hydrates to gaseous propane and water. This study, an important one in the field of heat transfer, indicated that the rate of heat transfer could be correlated with an expression that incorporates the driving force for dissociation expressed

as a temperature difference. The dissociation of methane hydrates was found to behave similarly and was also modeled as a heat-transfer-controlled process (Kamath et al. 1987). Ullerich (1987) also modeled the hydrate dissociation process on the basis of heat-transfer consideration, but they viewed it as a moving boundary ablation process.

Kim et al. (1987) suggested that the hydrate dissociation rate is proportional to the driving force that is defined as the difference between the fugacity of methane at the hydrate-vapor-liquid water equilibrium conditions and the fugacity in the bulk of the gas phase. This model was used by Jamalludin et al. (1989) to describe the dissociation of a methane hydrate block under thermal stimulation. It was shown that by changing the pressure we could move from a heat-transfer-controlled regime to one where both heat transfer and intrinsic kinetics are important.

Selim et al. (1989 and 1990) proposed a model for the hydrate dissociation in porous media based on heat and mass transfer. The model viewed the dissociation as a process whereby gas and water were produced at a mixing boundary, which separated the dissociated zone from the undissociated zone.

From the theoretical viewpoint, Bishnoi et al. (1996) viewed hydrate dissociation was a sequence of lattice destruction and gas desorption processes. The process of heat transfer during hydrate dissociation was analogous to nucleate boiling phenomena.

1.3 Significance of This Work

Comparing to methane, and ethane hydrate formation and dissociation, the reaction rates and relevant kinetic behavior of PGH formation and dissociation are still not well known, especially in the porous sediments.

In our research work, the PGH formation reaction was carried out in batch reactor under the conditions of $P=0.427$ MPa and $T=273.5$ K. It means that no ice can form inside the reactor, and the mass balance of propane between PGH formation and dissociation reactions can be easily established, because the formation pressure (0.427 MPa) is lower than the condensation pressure of propane gas (0.456 MPa) at given temperature (273.5 K).

The reactions of PGH formation and dissociation in this work were accomplished under the isothermal condition. Therefore, the effect of temperature could be ignored. Samples of cylindrical cage with homogeneous dispersion of water in the porous sediments were carefully prepared and used in our work. So the formation and dissociation reactions of PGH should be much more smooth and homogeneous than those of methane gas hydrate in sandstone samples done by Yousif et al. (1991a and b).

PGH dissociation reaction in this work was carried out by depressurization that is frequently used in industry gas production from natural gas hydrates, instead of the heating process that is frequently used by many researchers in laboratory.

Kamath et al. (1984) studied the PGH dissociation in the reaction system of propane (g), water (l), and PGH (s) by using the heating process.

The importance of studying the kinetic behavior of the PGH formation and dissociation within porous sediments is coming from the fact that PGH existing either in

permafrost or in deep-sea sediments are mixtures with various sediments, and not just pure solid hydrates. The PGH formation and dissociation in bulk water-gas system can not exactly represent the actual kinetic behavior of the hydrate samples existing in nature.

Our work not only focused on the study of kinetic behavior of PGH formation and dissociation, but also on the mass balance of propane between PGH formation and dissociation process. Our work also can provide more information for the future research on hydrate kinetic behavior of methane, ethane, and natural gas mixture.

CHAPTER 2: LITERATURE REVIEW RELATED TO PROPANE GAS HYDRATE (PGH)

2.1 Background of PGH Chemistry and Thermodynamic Property

From the chemistry viewpoint, propane gas hydrate (PGH) is a clathrate crystalline compound. Through hydrogen bonding, water molecules form frameworks containing relatively large cavities, which can be occupied by certain gas molecules, whose molecular diameters are less than the diameter of the cavities. PGH crystallizes in structure II due to the larger diameter of propane gas molecule. The formation of PGH is a non-stoichiometric, exothermic reaction between gas and water, and can be represented by the equation (1).

Where the number of 17 is called the hydration number (the number of water molecules per one gas molecule), and ΔH is the heat of reaction.

Figure 4 (Sloan 1998) shows the temperature-pressure phase diagram for propane-water system, which indicates clearly the zones of PGH formation and dissociation. In this figure, the co-ordinate (T_e , P_e) indicates the equilibrium temperature-pressure for PGH formation where the co-ordinate (T_f , P_f) in region 2 indicates the operating condition in this work.

The PGH dissociation process is just the reverse process of PGH formation. When the pressure is lower than the equilibrium pressure at given temperature (273.5 K) or the temperature is higher than the equilibrium temperature at given pressure, the dissociation of the PGH can take place. The region 3 in **Figure 4** is the PGH dissociation zone. The

PGH dissociation is an endothermic reaction, and can be accomplished by either depressurization or heating process.

- 1: C_3H_8 (l), C_3H_8 (g), H_2O (l), PGH (s)
- 2: C_3H_8 (g), H_2O (l), PGH (s)
- 3: C_3H_8 (g), H_2O (l)

Figure 4 Pressure-Temperature Phase Diagram for Propane Gas-Water System (Sloan 1998)

2.2 PGH Formation Rate and Relevant Kinetic Behavior

Even for the formation reaction rates of methane or ethane gas hydrates, for which several papers were published by e.g., Vysniauskas et al. (1983 and 1985), Englezos et al. (1987a and b), Bishnoi et al. (1996), all the above past papers measured the overall methane or ethane gas hydrate formation rates without using sediments. Therefore, the boundary between reacting three phases (methane (g), water (l), methane or ethane gas hydrate (s)) could not be well defined and the experimental reproducibility remained questionable.

Kono et al. (2001) investigated the kinetics of methane hydrate formation in porous sediments (such as different size of glass beads). They reported the overall kinetic rate constants of methane gas hydrate formation through many experimental data, and a reaction engineering rate equation of the quasi-first order for the methane gas hydrate formation, where the rate constant (k_f) was practically as a function of the pressure, temperature, and sediment type. This paper is the first one to systematically study the kinetics of methane gas hydrate formation in porous sediments through experiments.

2.3 PGH Dissociation Rate and Relevant Kinetic Behavior

The dissociation was initiated by a drop in the pressure to a desired pressure below the three-phase equilibrium pressure at a constant temperature. The amount of gas evolved from the dissociating hydrates was obtained as a function of time.

For the measurement of hydrate dissociation without sediments, only the dissociation by the heating process (by changing temperature) has been reported on a laboratory scale in the past literatures.

Kamath et al. (1984) developed an experimental technique to obtain PGH dissociation rates by measuring the heat transfer to a solid PGH phase. They assumed the heat transfer is the rate-determining step, which seems to be not appropriate. In 1987, Kamath et al studied the methane hydrate dissociation by using the same method as shown above.

Yousif et al. (1991a and b) carried out the process of methane gas hydrate dissociation in Berea sandstone samples by depressurization at a constant bath temperature. However, they could not control the homogeneity of water dispersion within the sandstone. Therefore, the methane gas hydrate dissociation behavior became much more complicated. Only qualitative experimental data were published.

Kono et al. (2001) investigated the methane gas hydrate dissociation in porous sediments by depressurization. Two types of dissociation behavior were observed, depending on the type of sediments used. In some cases, the dissociation followed a zero-order reaction rate while in others a first order reaction rate was observed.

As could be seen from the previous works, most researchers focused on the methane and ethane gas hydrates, very few past papers studied on the PGH formation and dissociation, especially in the porous sediments. The importance of studying the kinetic behavior of PGH formed within porous sediments is coming from the fact that PGH existing either in permafrost or in deep-sea sediments are the mixtures with various sediments and not just pure solid hydrates, and that mass transfer of propane gas is easily controlled. The PGH formation and dissociation in bulk water-gas system can not exactly represent the actual kinetic behavior of the hydrate samples existing in nature. Therefore we decided to study the reaction rates and relevant kinetic behaviors of PGH formation and dissociation.

CHAPTER 3: EXPERIMENT

3.1 Experimental Equipment

In order to achieve our research objectives, the custom-design and custom-built packed bed reactor was used, in which the PGH formation and dissociation reactions could have been carried out under almost isothermal condition. **Figure 5** shows the sketch of the experimental apparatus for PGH formation and dissociation on kinetic behavior studies.

As shown in **Figure 5**, the reactor system consists of a cylindrical reactor with the inner diameter of $\frac{3}{4}$ inch and the height of 14 inch, a thermistor with a high accuracy (± 0.1 K), three pressure gauges, three control needle valves, one custom-built propane gas receiver with the inner diameter of 2 inch and height of 40 inch, and flow pipelines made of stainless steel SS304 with a diameter of $\frac{1}{4}$ inch.

Two pressure gauges of (6) and (10) with accuracy of ± 5 psig shown in **Figure 5** were used for PGH formation and one pressure gauge of (4) with accuracy of ± 1 psig for PGH dissociation.

High purity propane gas (99.90%) and water were used to form PGH. The propane gas entered the bottom of the reactor through a high-pressure regulator and a needle valve connected in series.

Several different sizes of spherical glass beads (such as $D_p=75\sim 150\ \mu\text{m}$, $200\sim 280\ \mu\text{m}$, and $460\sim 560\ \mu\text{m}$) were chosen as sediments in our work. The wet sediment sample inside the reactor was hold by a custom-designed cage with a diameter of 0.63 inch and length of 12 inch.

Figure 5 Experimental equipment for the formation and dissociation of propane gas hydrate with sediments

3.2 Experimental Procedure

3.2.1 PGH Formation

The reaction system used in this study consists of C_3H_8 (gas), H_2O (liquid), PGH (solid), and sediments (solid). In order to study PGH formation, the procedures before starting the PGH formation are that (1) known amount of water was uniformly distributed within known amount of dry sediments (glass beads) in a separate container, (2) the wet sediments were fed into the custom-designed cage, (3) the same sediments (dry sediments mixed with water) were put into the reactor. Before starting the PGH formation reaction, the leakage of reactor should be checked. Then the reactor was completely cooled down to attain the temperature at 273.5 K by using isothermal bath. The volume of the isothermal bath was much larger than that of the reactor by more than 50 times, so that the heat of reactions evolved during the exothermic PGH formation did not really affect the reactor temperature. The PGH formation could be assumed as an isothermal reaction

Once the designed temperature (273.5 K) was reached, the high purity of propane gas was fed into the reactor from the bottom of the reactor as shown in **Figure 5**. The initial operation pressure for the PGH formation was higher than the equilibrium pressure at the operation temperature, which was kept constant at 273.5 K during the operation. The purpose of the thermistor is to continuously monitor the inner temperature (this temperature is always higher than 273 K) and confirm isothermal reacting condition. Since the inner reactor temperature was maintained at $T > 273$ K, it is very clear that no ice should be formed.

Generally we set up the pressure to a certain value (0.427 MPa) at the beginning, and then stop feeding the propane gas, and kept the inner temperature at 273.5 K. As the

PGH formation went on, the pressure of the reactor should go down. The formation reaction was assumed to stop when the pressure almost kept constant. During the PGH formation process, the reaction pressure and the formation time were recorded. From the pressure change with formation time, the kinetic behavior of PGH formation could be predicted. The experiment was repeated by changing the particle size of glass beads and the water saturation degree (S) to assess the effect of the particle size and water saturation degree on the PGH formation reaction rates by using the same procedure as above.

3.2.2 PGH Dissociation

After the PGH formation was finished, we started doing the PGH dissociation experiments. The initial pressure of the dissociation (0.168 MPa) was slightly lower than the equilibrium pressure (0.175 MPa) at a constant temperature of 273.5 K. The experiments were carried out by depressurization in this study instead of by changing temperature as these researchers (Kamath et al. 1984). The pressure of the reactor gradually went down, and finally reached 0.1 MPa (absolute pressure). Meanwhile, we used a gas receiver to collect all the propane gas produced from the PGH and obtained a series of data, which was the volume change of the propane gas as a function of dissociation time. Meanwhile, the dissociation pressure was also recorded.

CHAPTER 4: EXPERIMENTAL RESULTS & DISCUSSION

4.1 PGH Formation

PGH formation experiments in this study were carried out in the isothermal batch reactor. The pressure change of the reactor is uniquely related to the extent of PGH formation reaction. Therefore, reaction rates and relevant kinetic behavior of PGH formation could be achieved by measuring the pressure change of reactor.

As shown in **Figure 6**, the value of V_R was measured by filling water into the empty reactor; the value of V_{H_2O} was measured by weight of water; the value of V_s was obtained by measuring the weight, the density and the porosity of glass beads, and the value of V_{PB} was obtained by measuring the diameter and the length of the packed bed. Other parameter values (such as $V_{I\text{gs}}$, $V_{\text{gs in PB}}$, and $V_{T\text{gs}}$) could be obtained by using the following equations of (2), (3), and (4).

Figure 6 Schematic reactor of PGH formation in porous sediments in this study

$$V_R = V_{I\text{ gs}} + V_{PB} \quad (2)$$

$$V_{PB} = V_{H_2O} + V_{gs\text{ in PB}} + V_s \quad (3)$$

$$V_{T\text{ gs}} = V_{I\text{ gs}} + V_{gs\text{ in PB}} \quad (4)$$

Where

$V_{gs\text{ in PB}}$: Volume of the gas space in packed bed [lit]

V_{H_2O} : Volume of water in porous sediments fed in at the beginning [lit]

$V_{I\text{ gs}}$: Volume of gas space [lit]

V_{PB} : Volume of the packed bed (cage) [lit]

V_R : Volume of the reactor [lit]

V_s : Volume of particles (sediments) [lit]

$V_{T\text{ gs}}$: Total volume of the gas space in the reactor [lit]

In our research work, the cage (packed bed) made of the plastic fibers was used to hold the mixture of sediments and water, the following basic equations of (5), (6), and (7) were used to determine the porosity of dry sediments (ε) and the water saturation degree (S) in porous sediments.

$$V_{\varepsilon} = V_{PB} - V_s \quad (5)$$

$$\varepsilon (\%) = \frac{V_{\varepsilon}}{V_{\varepsilon} + V_s} \quad (6)$$

$$S = \frac{V_{H_2O}}{V_{gs \text{ in PB}} + V_{H_2O}} \quad (7)$$

Where

ε : Porosity of sediments under dry condition [-]

V_{ε} : Volume of voids in dry sediments [lit]

S: Water saturation degree [%]

The mole amount of propane gas ($N_g(t)$) in the reactor at any time is a function of the pressure, temperature and the volume of gas space inside the reactor, and could be calculated from the equations of (8), and (9).

$$N_g(t) = \frac{V_{T \text{ gs}}}{v(t)} \quad (8)$$

$$v(t) = \frac{zRT}{P(t)} \quad (9)$$

Where

$N_g(t)$: Mole amount of propane gas left in the reactor at time t [mole]

$v(t)$: Specific volume of propane gas in the reactor at time t [lit/mole]

$P(t)$: Reactor pressure at time t [MPa]

z : Compressibility factor [-]

T : Reactor temperature [K]

The mass balance equations of (10) and (11) were used to calculate the mole amount of PGH ($n_H(t)$) formed and $n_g(t)$ (defined in equation (11)) during the formation process respectively.

$$n_0 = n_H(t) + N_g(t) \quad (10)$$

$$\frac{n_{H_2O}}{17} = n_H(t) + n_g(t) \quad (11)$$

Where

n_0 : Total mole amount of propane gas fed in at time $=0$ [mole]

$n_g(t)$: Mole amount of propane gas in the reactor defined in equation (11) [mole]

$n_H(t)$: Mole amount of PGH formed at time t [mole]

n_{H_2O} : Mole amount of water fed in the reactor at the beginning [mole]

The PGH formation reaction rate could be expressed by the equation (12).

$$-\frac{1}{V_{H_2O}} \frac{dn_g(t)}{dt} = k_f (n_g(t))^{n^*} \quad (12)$$

Where

k_f : Overall reaction rate constant [$\text{lit}^{-1} \text{hr}^{-1}$]

n^* : Overall order of the formation reaction [mole]

The overall formation reaction constant k'_f (hr^{-1}) is defined as $V_{H_2O} k_f$ in this study.

From the PGH formation experimental data recorded, the pressure change with time was obtained, and then the change of n_H with time could be obtained by using the above equations. Furthermore, the kinetic behavior of PGH formation in porous sediments (such as the overall order of the reaction, n^* , and the overall reaction rate constant, k_f) could be obtained.

Table 1 shows the summary of operating conditions of PGH formation in porous sediments

Table 1 Summary of experimental operating conditions of PGH formation
at the pressure of 0.427 MPa and the temperature of 273.5 K

Run#	Particle size (D_p) [μm]	Porosity (dry) ε [%]	Water saturation degree (S) [%]
1	75~150	42.8	30.1
2	75~150	42.8	15.0
3	200~280	42.0	53.4
4	200~280	42.0	30.1
5	200~280	42.0	15.1
6	460~560	40.8	30.2
7	400~560	40.8	15.2

The following figures (**Figure 7~Figure 13**) show that the overall formation reaction rates are of quasi-first order ($n^*=1$). The formation reaction rate constants were different for each experiment, based on both the particle sizes (D_p) and the water saturation degree

(S). This result is very well in agreement with the result of our last year's work on the methane gas hydrate formation in porous sediments.

Figure 7 n_g and the formation pressure as a function of time in porous sediments with respect to $D_p = 75 \sim 150 \mu\text{m}$ and $S = 30.1\%$

Figure 8 n_g and the formation pressure as a function of time in porous sediments with respect to $D_p=75\sim150\ \mu\text{m}$ and $S=15.0\%$

Figure 9 n_g and the formation pressure as a function of time in porous sediments with respect to $D_p=200\sim280\ \mu\text{m}$ and $S=53.4\%$

Figure 10 n_g and the formation pressure as a function of time in porous sediments with respect to $D_p=200\sim280\ \mu\text{m}$ and $S=30.1\%$

Figure 11 n_g and the formation pressure as a function of time in porous sediments with respect to $D_p=200\sim 280\ \mu\text{m}$ and $S=15.1\%$

Figure 12 n_g and the formation pressure as a function of time in porous sediments with respect to $D_p=460\sim560\ \mu\text{m}$ and $S=30.2\%$

Figure 13 n_g and the formation pressure as a function of time in porous sediments with respect to $D_p = 460 \sim 560 \mu\text{m}$ and $S = 15.2\%$

Typical values of reaction rate constants (k'_f , hr^{-1}) of PGH formation for each experiment have been already shown in the above figures (**Figure 7~Figure 13**). Here, it should be very clearly understood that these reaction rate constant values were not the intrinsic rate constant of a chemical reaction. But these values were the overall reaction rate constants, including the effect of many factors (such as mass transfer, heat transfer, sediment properties).

It was found that the overall reaction rate constant (k'_f , hr^{-1}) increased with increase of the particle size if the water saturation degree was the same (such $S=30\%$, 15%). Once the water saturation degree was fixed, the gas space between the particles increased with increase of the particle size, as a result the diffusion coefficient increased and caused the reaction rate increased.

It was also found that the overall reaction rate constant (k'_f , hr^{-1}) increased with decrease of water saturation degree (S) if the particle size was the same (such as $D_p=75\sim150\ \mu\text{m}$, $200\sim280\ \mu\text{m}$, and $460\sim560\ \mu\text{m}$). In this case, the gas space between the particles increased with decrease of water saturation degree (S), the propane gas could even more easily pass through these gas spaces between particles, and furthermore increased the reaction rate of PGH formation. The values of overall reaction rate constants reflected, to some extent, how fast the PGH formation reaction was. The larger the overall reaction rate constant was the faster the PGH formation reaction. Our experimental results provided a strong support on this point.

However, it was found through the experiments that the particle size (D_p) and the water saturation degree (S) have a significant effect on the PGH formation in porous

sediments, and the nucleation process is not important in our reaction system. These results had already been verified by our last year's work on methane gas hydrate formation in porous sediments.

In our research work, the PGH formation was carried out under the isothermal condition in packed bed batch reactor, the formation pressure acted as a major driving force during the formation process, so the pressure change with time practically reflected the PGH formation kinetic behavior.

Figure 14~Figure 20 show the formation pressure as a function of time for PGH formation in porous sediments with respect to different sediment's particle sizes (such as $D_p=75\sim150\ \mu\text{m}$, $200\sim280\ \mu\text{m}$, and $400\sim560\ \mu\text{m}$), and different water saturation degree (such as $S=50\%$, 30% , and 15%) respectively. **Figure 14~Figure 15** show that PGH formation reaction for the smaller particle size (such as $D_p=75\sim150\ \mu\text{m}$) smoothly took happen. But **Figure 16~Figure 20** show that PGH formation reaction for larger particle size (such as $D_p=200\sim280\ \mu\text{m}$, and $400\sim560\ \mu\text{m}$) seems to consist of two reaction steps, one is controlled by the intrinsic chemical reaction, and another is mainly affected by the mass transfer.

Figure 14 Formation pressure as a function of time for PGH formation in porous sediments with respect to $D_p=75\sim 150$ μm and $S=30.1\%$

Figure 15 Formation time as a function of time for PGH formation in porous sediments with respect to $D_p=75\sim150\ \mu\text{m}$ and $S=15.0\%$

Figure 16 Formation pressure as a function of time for PGH formation in porous sediments with respect to $D_p=200\sim 280\ \mu\text{m}$ and $S=53.4\%$

Figure 17 Formation pressure as a function of time for PGH formation in porous sediments with respect to $D_p=200\sim 280\ \mu\text{m}$ and $S=30.1\%$

Figure 18 Formation pressure as a function of time for PGH formation in porous sediments with respect to $D_p=200\sim 280\ \mu\text{m}$ and $S=15.1\%$

Figure 19 Formation pressure as a function of time for PGH formation in porous sediments with respect to $D_p=460\sim560\ \mu\text{m}$ and $S=30.2\%$

Figure 20 Formation pressure as a function of time for PGH formation in porous sediments with respect to $D_p=460\sim560\ \mu\text{m}$ and $S=15.2\%$

4.2 PGH Dissociation

PGH dissociation was carried out by depressurization starting at a pressure of 0.168 MPa under the isothermal condition of $T=273.5$ K. The overall dissociation reaction rate constant (k_d) was experimentally found to be a function of pressure, particle size (D_p), and water saturation degree (S).

During the PGH dissociation process, the volume change of propane gas generated from PGH was recorded, so the change of mole amount of the propane gas generated from PGH with time t can be obtained by using the equation (13).

$$P V_{C_3H_8}(t) = n'_g(t) RT_{room} \quad (13)$$

Where

$n'_g(t)$: Total mole amount of propane gas generated from PGH at time t [mole]

P : Pressure of propane gas in the gas receiver [MPa]

T_{room} : Temperature of gas receiver [K]

$V_{C_3H_8}(t)$: Volume of propane gas generated from PGH at time t [lit]

The mass balance could be established by the equation (14) for PGH dissociation.

$$n'_0 = n'_H(t) + n'_g(t) \quad (14)$$

Where

n'_0 : Total mole amount of PGH in the reactor at time=0 [mole]

$n'_H(t)$: Mole amount of PGH left in the reactor at time t [mole]

The dissociation reaction rate of PGH in porous sediments could be expressed by the equation (15).

$$-\frac{1}{V_{H_2O}} \frac{dn'_H(t)}{dt} = k_d (n'_H(t))^{n^\#} \quad (15)$$

Where

k_d : Dissociation reaction rate constant [$\text{lit}^{-1} \text{hr}^{-1}$]

$n^\#$: The order of the dissociation reaction [mole]

The overall dissociation reaction constant k'_d (hr^{-1}) is defined as $V_{H_2O}k_d$ in this study.

The change of PGH left in the reactor as a function of time could be obtained by using equation (13) and (14). Furthermore, the kinetic behavior of PGH dissociation was obtained (such as the overall dissociation reaction rate constant, k_d , and the overall order of the dissociation reaction, $n^\#$).

Table 2 shows the summary of operating conditions of PGH dissociation in porous sediments for each experiment

Table 2 Summary of experimental operating conditions of PGH dissociation
at the pressure of 0.168 MPa and the temperature of 273.5 K

Run#	Particle size (D_p) [μm]	Porosity (dry) ε [%]	Water saturation degree (S) [%]
1	75~150	42.8	30.1
2	75~150	42.8	15.0
3	200~280	42.0	53.4
4	200~280	42.0	30.1
5	200~280	42.0	15.1
6	460~560	40.8	30.2
7	400~560	40.8	15.2

The following figures (**Figure 21~Figure 22**) show that the overall dissociation reaction rates are of quasi-first order ($n^*=1$). The dissociation reaction rate constants were different for each experiment, based on both the particle sizes (D_p) and the water saturation degree (S). This result is very well in agreement with the result of our last year's work on the methane gas hydrate dissociation in porous sediments.

Figure 21 Mole amount of propane gas generated fro PGH as a function of time in porous sediments with respect to $D_p=75\sim 150\ \mu\text{m}$ and $S=30.1\%$

Figure 22 Mole amount of propane gas generated from PGH as a function of time in porous sediments with respect to $D_p=75\sim150\ \mu\text{m}$ and $S=15.0\%$

Figure 23 Mole amount of propane gas generated from PGH as a function of time in porous sediments with respect to $D_p=200\sim 280\ \mu\text{m}$ and $S=53.4\%$

Figure 24 Mole amount of propane gas generated from PGH as a function of time in porous sediments with respect to $D_p=200\sim 280\ \mu\text{m}$ and $S=30.1\%$

Figure 25 Mole amount of propane gas generated from PGH as a function of time in porous sediments with respect to $D_p=200\sim 280\ \mu\text{m}$ and $S=15.1\%$

Figure 26 Mole amount of propane gas generated from PGH as a function of time in porous sediments with respect to $D_p=460\sim560\ \mu\text{m}$ and $S=30.2\%$

Figure 27 Mole amount of propane gas generated from PGH as a function of time in porous sediments with respect to $D_p=460\sim560\ \mu\text{m}$ and $S=15.2\%$

Typical values of reaction rate constants (k'_d , hr^{-1}) of PGH dissociation for each experiment have already been shown in the above figures (**Figure 21~Figure 27**). It should be very clearly understood that these reaction rate constant values are not the intrinsic rate constant of a chemical reaction. On the other hand, these values are the overall reaction rate constants including the effect of many factors (such as mass transfer, heat transfer, sediment properties).

It was found that the overall dissociation reaction rate constant (k'_d , hr^{-1}) for each experiment (Run#1-Run#7) was different, based on the different particle size (such as $D_p=75\sim150\ \mu\text{m}$, $200\sim280\ \mu\text{m}$, and $460\sim560\ \mu\text{m}$) and the different water saturation degree ($S=50\%$, 30% , and 15%). These two parameters do really affect the dissociation reaction rate of PGH in sediments.

CHAPTER 5: CONCLUSION

Based on our experimental works, the following conclusions were obtained.

1. The formation and dissociation reaction rates and their kinetic behavior of propane gas hydrate (PGH) within the well-defined sediment particle's packing structures were experimentally investigated by using a multi-phase heterogeneous reaction system, consisting of propane gas (g), water (l), PGH (s) and sediment particles (glass beads) (s).
2. The formation reactions were carried out under the conditions of $P=0.427$ MPa and $T=273.5$ K, and the dissociation reaction under the conditions of $P\leq 0.168$ MPa and $T=273.5$ K.
3. A custom designed packed bed reactor was used for the kinetic analysis of the above defined PGH reaction system under the smooth operating conditions, yielding the satisfactory, reproducible material balance.
4. Quantitative formation and dissociation overall reaction rates were derived and their orders of the reactions were experimentally obtained. The effects of the major parameters, such as the primary sediment particle sizes, porosity, and water saturation degree on the reaction mechanisms were obtained experimentally.
5. The overall reaction rate constant of PGH formation was significantly affected by the particle size and the water saturation degree. Here it should be well understood that these overall reaction rate constants of PGH formation were not identical with the intrinsic rate constant of a chemical reaction, but including at least the effect of gas mass transfer.

6. The dissociation reaction rates in this study were measured by depressurization method, and also affected by the particle size and the water saturation degree.

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