

Phase Equilibrium Conditions of Gas Hydrates for Natural Gas Solid Transportation and Storage

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ABSTRACT: Natural gas hydrates are ice-like solid substances, which are composed of water and natural gas, mainly methane. They have three kinds of crystal structures of five polyhedra formed by hydrogen-bonded water molecules, and are stable at high pressures and low temperatures. They contain large amounts of organic carbon and widely occur in deep oceans and permafrost regions. Therefore, they are expected as a potential energy resource in the future. Especially, 1m³ natural gas hydrate contains up to 172Nm³ of methane gas, depending on the pressure and temperature of production. Such large volumes make natural gas hydrates can be used to store and transport natural gas. In this study, three-phase equilibrium conditions for forming natural gas hydrate were numerically obtained in pure water. The results show that the predictions match the previous experimental values very well. And, help gases such that ethane, propane, i-butane, and n-butane reduce the hydrate formation pressure at the same temperature.

Keywords: Gas hydrate, Natural gas, Transportation, Storage, Phase equilibrium

1. INTRODUCTION

Siberian chemical plant in 1,930's had frequent blocking problem in the transportation pipeline of natural gas. The cause of such problem was attributed by the combination of gas and water in the pipe that produce hydrate, which adhered to inner pipe wall. The natural gas hydrate was taken attention by this discovery [4]. More than 99% of naturally produced natural gas hydrate consists of methane, and is widely dispersed in the continental slope and continental Shelf of the Pacific and the Atlantic, the Antarctica etc. The reserve of

fossil fuel is 500 billion carbon ton and the reserve of methane is 360 million carbon ton. The reserve of gas hydrate is more than 1 trillion carbon ton, which is twice the fossil fuel [1,6]. Therefore, natural gas hydrate as a kind of gas hydrate is expected to replace fossil fuel as new energy source of 21st century. Also 1 m³ hydrate of pure methane can be decomposed to the maximum of 216 m³ methane at standard condition and 1 m³ hydrate of natural gas can be decomposed to 180 m³ natural gas at standard condition [8]. If these characteristics of hydrate are reversely utilized, natural gas is fixed into water in the form of hydrate solid. Therefore,

the hydrate is considered to be a great way to transport and store natural gas in large quantity. Especially the transportation cost is known to be 18-24% less than the liquefied transportation [3,10].

Gas hydrate is formed by physical binding between water molecule and gas such as methane, ethane, propane, or carbon dioxide, etc., which is captured in the cavities of water molecule under the specific temperature and pressure. The hydrate (Fig. 1) is a solid container similar to ice, of which crystal structure is polyhedron cavity to consist of water molecule by hydrogen bond, and it is expressed as n^m . For example, $5^{12}6^2$ means 14 cavities with 12 pentagons and 2 hexagons. 5^{12} , $5^{12}6^2$, $5^{12}6^4$, $5^{12}6^8$, and $4^35^66^3$ are so far recognized as cavity type. Structure I (Fig. 2) is a combination of 6 polyhedrons($5^{12}6^2$) containing 14 facets with 2 polyhedrons(5^{12}) containing 12 facets, structure II (Fig. 3) is a combination of 16 polyhedrons(5^{12}) containing 12 facets with 8 polyhedrons($5^{12}6^4$) containing 16 facets, and

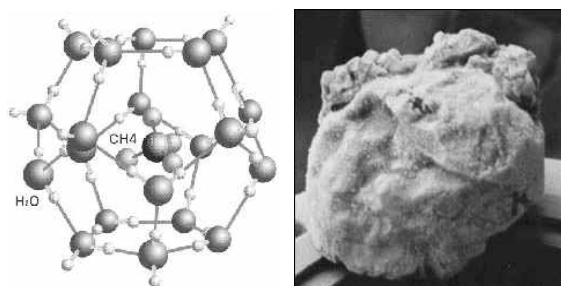


Figure 1: Natural gas hydrate.

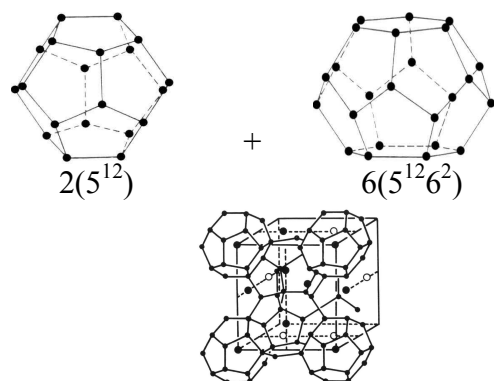


Figure 2: Crystalline lattice of natural gas hydrate, structure I.

structure H in Figure 4 is a combination of 3 polyhedrons(5^{12}) containing 12 facets with 2 polyhedrons($4^35^66^3$) containing 16 facets and 1 polyhedron ($5^{12}6^8$) containing 20 facets [5,9].

Since natural gas is a mixed gas, its hydrate structure depends on its composition. If the natural gas containing more than 10% ethane forms structure I but has the characteristics of structure II. And the mixed gas containing more than 0.108% n-butane forms structure II but has the characteristics of structure I. On the other hand, the natural gas containing more than 0.0146% propane and 0.01% i-butane forms structure II, and the natural gas with more than 0.866% i-pentane forms structure H. Because the natural gas including n-pentane cannot form any hydrates, n-pentane does not affect the structure of hydrate.

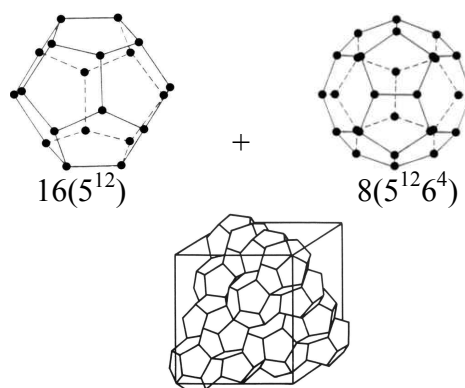


Figure 3: Crystalline lattice of natural gas hydrate, structure II.

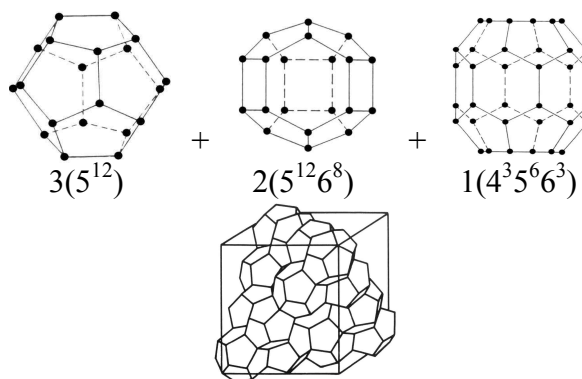


Figure 4: Crystalline lattice of natural gas hydrate, structure H.

Carbon dioxide form structure I regardless of composition ratio and nitrogen can form structure I or II depending on the formation temperature or pressure [7]. However, the gas of large molecular weight affects its structure when it forms hydrate of mixed gas. Also, its hydrate formation condition depends on its composition

Therefore, in this study, we focus on the formation conditions of methane hydrate added helping gas and imported natural gases in Korea.

2. THERMODYNAMIC MODEL

In a system with N substances from which only Nh are present in the hydrate crystal lattice, equilibrium among the gas(V), the liquid(L), and the hydrate(H) phases is represented, using fugacities, by

$$f_i^V = f_i^L \quad i = 1, 2, \dots, N \quad (1)$$

$$f_j^H = f_j^L \quad i = 1, 2, \dots, N_h \quad (2)$$

where

$$f_i^V = y_i \phi_i P \quad (3)$$

where y_i and ϕ_i denote the mole fraction and the fugacity coefficient for component i at a pressure P. The fugacity coefficient is computed from an expression based on the equation of state. In the present work, The RKS-EOS incorporated with the modified MHV2 mixing rule was used. Also, electrolytes are known to be excluded from the hydrate crystal lattice and the vapor phase. Hence, the van der Waals-Platteeuw statistical thermodynamics model can be used to describe the hydrate phase. This model is incorporated by vapor-liquid equilibrium so that the Nh equations (2) are replaced by the following single equation.

$$f_w^H = f_w^L \quad (4)$$

The fugacity of water in the hydrate is given by

$$f_w^H = f_w^{MT} \exp\left(\frac{\Delta\mu_w^{MT-H}}{RT}\right) \quad (5)$$

where f_w^{MT} is the fugacity of water in the empty hydrate lattice, and the quantity $\Delta\mu_w^{MT-H}$ denotes the difference between the chemical potential of water in the empty hydrate lattice (μ_w^{MT}) and that in the hydrate phase (μ_w^H) and is described by the following equation.

$$\frac{\Delta\mu_w^{MT-H}}{RT} = \sum_{m=1}^K \nu_m \ln\left(1 + \sum_{j=1}^{N_h} C_{mj} f_j\right) \quad (6)$$

where m denotes cavities which guest molecules can occupy, and ν_m is the number of cavities of type m per water molecule in the hydrate lattice given in Table I. C_{mj} is the Langmuir constant for the m th kind of cavities, and f_j is the fugacity of the gas component j in the hydrate phase. The Langmuir constant with the spherically averaged cell potential function, $W(r)$, at a distance, r, from the center of cavity is given by

$$C_{mj} = \frac{4\pi}{kT} \int_0^R \exp\left(-\frac{\omega(r)}{kT}\right) r^2 dr \quad (7)$$

where

$$\omega(r) = 2z\varepsilon \left[\frac{\sigma^{12}}{R_r^{11}} \left(\delta^{10} + \frac{a}{R} \delta^{11} \right) - \left(1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right] \quad (8)$$

$$\delta^N = \frac{1}{N} \left[\left(1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right] \quad (9)$$

where z is the coordination number of the cavity, ε is the maximum attractive potential, σ is the core distance at zero potential, R is the free cavity radius, a is the radius of the spherical core, and N is 4, 5, 10, or 11. The

optimized Kihara potential parameters (a , σ , ε/k) used in this calculation were listed in Table I. The fugacity of water in the empty hydrate lattice is given by

$$f_w^{MT} = f_w^{L^0} \exp\left(\frac{\Delta\mu_w^{MT-L^0}}{RT}\right) \quad (10)$$

where $f_w^{L^0}$ is the fugacity of pure liquid water which is calculated by using the RKS-EOS, and the chemical potential difference of water between empty hydrate lattice and the pure liquid, $f_w^{L^0}$, is given by Holder et al.

$$\frac{\Delta\mu_w^{MT-L^0}}{RT} = \left(\frac{\Delta\mu_w^0}{RT^0}\right) - \int_{T^0}^T \left(\frac{\Delta h_w^{MT-L^0}}{RT^2}\right) dT + \int_0^P \left(\frac{\Delta v_w^{MT-L^0}}{RT}\right) dP \quad (11)$$

where

$$\Delta h_w^{MT-L^0} = \Delta h_w^0 + \int_{T^0}^T [38.12 - 0.141(T - 273.15)] dT \quad (12)$$

In the above equations, $\Delta\mu_w^0$ is an experimentally determined quantity which denotes the difference between the chemical potential of the empty hydrate lattice and the pure liquid water at 273.15K and zero absolute pressure, $\Delta v_w^{MT-L^0}$ denotes the volume difference between the empty hydrate lattice and the liquid water, and Δh_w^0 is the enthalpy difference between the empty hydrate lattice and the pure liquid water at $T^0 = 273.15K$ and zero absolute pressure. These parameters, in this work, reported by Parrish and Prausnitz (1972) were used and shown in Table II.

3. EXPERIMENTAL APPARATUS

Figure 5 shows schematic diagram for the experimental apparatus. 600 mL reactor (1) and 1.5 L supplemental tanks (24, 27) are manufactured with SUS316 to endure pressure of 30 MPa and salt erosion.

Table I : Kihara potential parameter.

Component	ε/k (K)	σ (Å)	a (Å)
CH ₄	154.54	3.1650	0.3834
C ₂ H ₆	176.40	3.2641	0.5651
C ₃ H ₈	203.31	3.3093	0.6502
i-C ₄ H ₁₀	225.16	3.0822	0.8706
n-C ₄ H ₁₀	209.00	2.9125	0.9379
i-C ₅ H ₁₂	307.09	3.2955	0.9868
N ₂	125.15	3.0124	0.3526
CO ₂	168.77	2.9818	0.6805

Table II : Parameters of s I and s II.

Parameters	s I	s II
$\Delta\mu_w^0$ (J/mol)	1263	883.8
Δh_w^0 (J/mol)	1389	1025
$\Delta v_w^{MT-L^0}$ (L/mol)	0.0030	0.0034

Considering high pressure operations in the reactor, check valve (8) is installed at the rear side of the tube connected to the reactor in order to prevent the back-flow of gas and water. Sapphire glass (2) of diameter 80 mm is installed for visualization at front side and rear side of the reactor. Tube (7) is made of 2 m length in order to ensure full heat transfer between gas and water entering the reactor. In the case of MFC (Bronk-horst Hi-tech Co.), MFC (21, 0~1000 g/hr) for liquid, MFC (22, 0~60 L/min) for large gas quantity, and MFC (23, 0~1500 mL/min) for small gas quantity are installed separately. For the experimental precision, 97~98% of experimental pressure is controlled by MFC for large gas quantity and the remaining 2~3% by MFC for small gas quantity to reduce over pressure, which may be generated by instantaneous inflow of large quantity. Analog style Heise manometer (19, 0~350 kgf/cm², Heise Co.) and digital gauge (16, Sensys Co.), error range within 0.25% in pressure

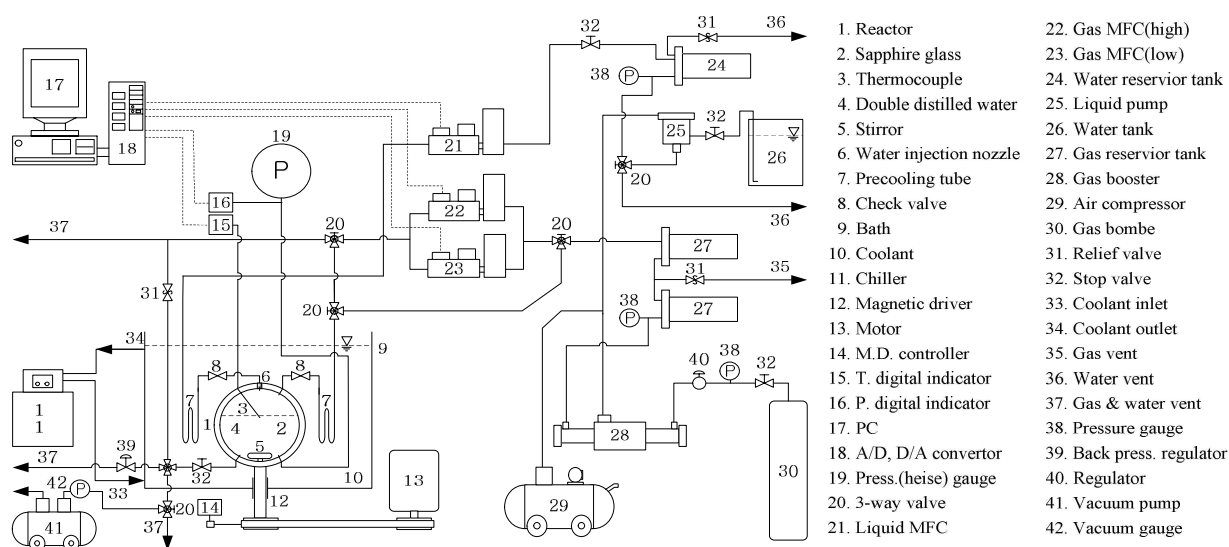


Figure 5: Schematic diagram of the apparatus.

measurement is used. 1/32 inch T-type heat transmitter (3, OMEGA Co.) and digital gauge (16, Sensys Co.) are used in the temperature measurement. Chiller (11, 228~403K, Jeio Tech Co.) for the control of reactor temperature, gas booster (28, 700 kg/cm², Schmidt, Kranz & Co GmbH) for high pressure gas, and PC (17) for the reading and recording of data such as pressure, temperature, and flow rate etc. are installed. Reactants were used in most experimentations are secondary distilled water and mixed gas (47, Rigas Co.). Table III shows the composition of reactant gases.

4. RESULT AND DISCUSSION

Hydrate is generally stable under high pressure and low temperature. It is easily decomposed to water and gas out of the stable region. Since the formation and decomposition of hydrate can be visually confirmed, phase equilibrium is performed considering the specialty of experimental apparatus. Model cases are isothermal experiment and isobaric experiment as shown in Figure 6. In the isothermal experiment, hydrate is formed at arbitrary temperature, B (T_{equ}) and pressure, A (P_{exp}), which is higher than pressure, D (P_{equ}), and

Table III: Compositions of reactant gases.

	Gas 1 (%)	Gas 2 (%)
Methane(CH ₄)	100	90.8784
Ethane(C ₂ H ₆)	0	5.63
Propane(C ₃ H ₈)	0	2.52
iso-Butane(i-C ₄ H ₁₀)	0	0.493
n-Butane(n-C ₄ H ₁₀)	0	0.447
iso-Pentane(i-C ₅ H ₁₂)	0	102PPM
Nitrogen(N ₂)	0	214PPM

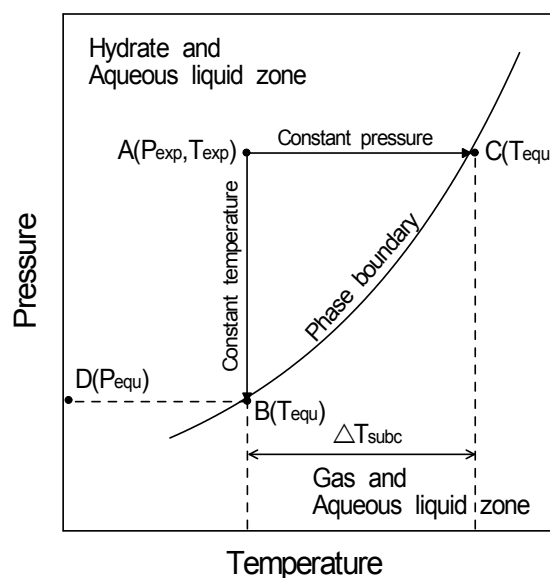


Figure 6: Experimental method.

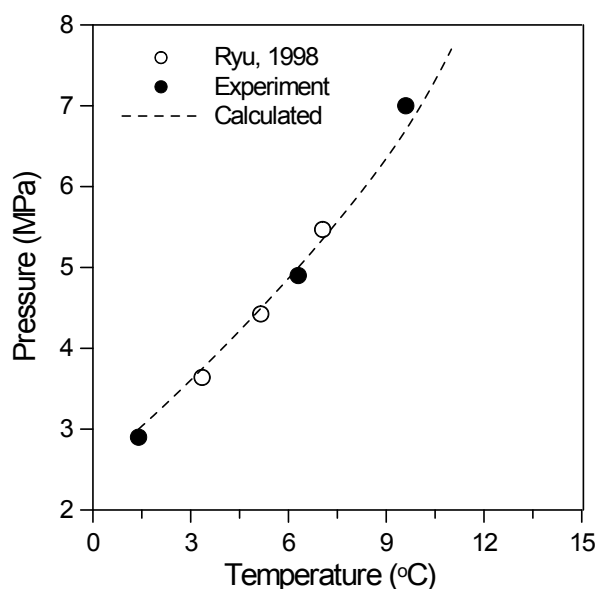


Figure 7: Comparison of calculated and experimental results using gas 1.

pressure is gradually decreased at constant temperature in the course, A→B. In the isobaric experiment, temperature is gradually increased at constant pressure in the course, A→C [2]. After performing two experiments in the present study, the isobaric experiment is found to be more convenient than the isothermal experiment. Since the decomposition of hydrate can be visually observed, the isobaric experiments have been performed in the following ways.

300 mL distilled water is poured into the reactor using a liquid phase pump and cooled to 274.15K, and experimental gas under 10 MPa is injected into the reactor at the pressure of 1 ~ 7 MPa according to experimental conditions. Experimental conditions (A) are kept constant for several hours in order to completely grow hydrate. After hydrate is fully grown, reactor temperature is raised by 0.1K for every two hours (A→C). The pressure increase due to the decomposition of hydrate is controlled to keep constant by discharging (37) gas within the reactor through the 3-way valve (20) and MFC.

Figure 7 and Figure 8 show the comparison of calculated and experimental data using gas 1 and gas 2. As shown in the figures, the

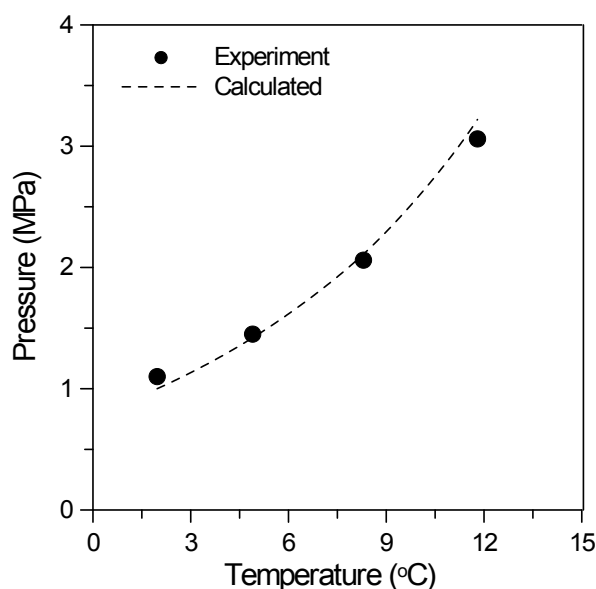


Figure 8: Comparison of calculated and experimental results using gas 2.

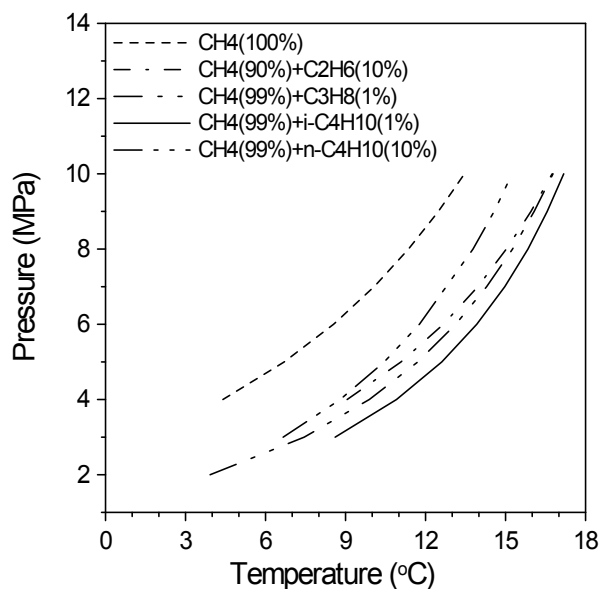


Figure 9: Equilibrium conditions of methane hydrate added help gas.

predictions match the previous experimental values very well. Therefore, the thermodynamic model using this study is proven to be adequate. Figure 9 shows the equilibrium conditions calculated the thermodynamic model of methane hydrate added help gas. As shown in the figure, help gases such that ethane, propane, i-butane, and n-butane reduce the hydrate formation

Table IV: Compositions of natural gas imported in Korea.

	CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₅ H ₁₂	n-C ₅ H ₁₂	N ₂	CO ₂
Indonesia	90.97	5.58	2.50	0.47	0.45	0.01	0.00	0.02	0.00
Malaysia	90.29	5.23	3.11	0.66	0.52	0.00	0.00	0.19	0.00
Brunei	90.21	5.14	3.02	0.67	0.88	0.03	0.01	0.04	0.00
Qatar	89.75	6.56	2.35	0.43	0.64	0.01	0.00	0.26	0.00
Oman	86.88	8.06	3.26	0.80	0.80	0.04	0.01	0.15	0.00
U.A.E	85.47	12.84	1.40	0.05	0.05	0.00	0.00	0.20	0.00
Australia	86.83	8.58	3.62	0.41	0.49	0.01	0.00	0.06	0.00

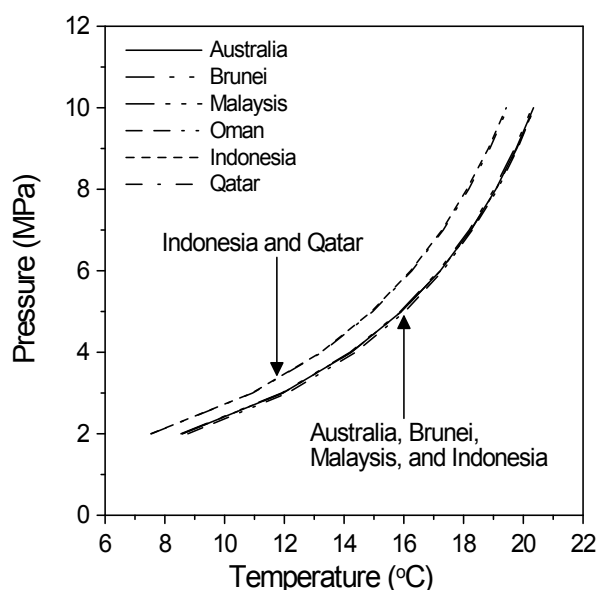
pressure at the same temperature. Especially, i-butane has the highest capability to decrease the formation pressure. Compositions of natural gas imported in Korea and equilibrium conditions calculated using the model are shown in Table IV and Figure 10, respectively. The figure shows that they have two groups one is Indonesia and Qatar, the other is Malaysia, Brunei, Oman, U.A.E, and Australia.

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**Figure 10:** Equilibrium conditions of natural gas imported hydrates in Korea.

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