

Determination of reference enthalpies and thermal expansivity using molecular dynamic simulations in the distortion model of gas hydrates

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(Received 8 March 2016 • accepted 20 June 2016)

Abstract—This work presents the determination of both reference chemical potential and temperature-dependent enthalpy changes of gas hydrates using molecular dynamics simulations. We introduced a method incorporating molecular dynamic (MD) simulations to the Lee-Holder distortion model for calculating the reference properties of single component structure II gas hydrates. The guest molecules affect the interaction between adjacent water molecules distorting the hydrate lattice, which requires diverse values of reference properties for different gas hydrates. We performed the simulation to validate the experimental data determining the reference chemical potential as well as the thermal expansivity of unit cell structure for structure II type gas hydrates. All simulations were performed using TIP4P water molecules at the reference temperature and pressure conditions. As an attempt to apply MD simulation to calculate the reference state of gas hydrate, we demonstrate lattice distortion of structure I and II gas hydrates. The reference chemical potential was generally found to increase with the size of the guest molecule. The temperature effect on the unit cell size, which will be used to calculate the enthalpy change of gas hydrate due to temperature, has been observed.

Keywords: Gas Hydrate, Reference Properties, Lattice Distortion

INTRODUCTION

Clathrate hydrates, also known as gas hydrates, are non-stoichiometric, crystalline molecular complexes formed from mixtures of water and low molecular weight gases, with the guest molecules occupying the interstices of polyhedral cages composed of strongly hydrogen bonded water molecules [1-4]. The encapsulation of the guest molecules is essential for the formation of hydrates; otherwise, the empty cage collapses into pure liquid or ice [4]. There are no chemical bonds between the gas (guest) and the water (host) molecules and the interaction is purely van der Waals type for most gas hydrates, while there is hydrogen bonding interaction between guest and host molecules for some gas hydrates [5]. There are a variety of guest molecules that can occupy the cavities, and their size, shape and nature determine the stability and the structure of the clathrate hydrate [4,6].

There is a dearth of experimental data on clathrate hydrate forming conditions [4,6-9]. Moreover, most thermodynamic models consider an empty hydrate cage that does not have a guest molecule as a reference state, which is highly unstable and is less likely to be determined experimentally [7,8]. On the contrary, computer simulations are performed close to equilibrium and for relatively short time periods and hence, play a pivotal role in determining averages of thermodynamic properties at stable states, thus acting

as a bridge between experimental results and theoretical calculations [7-9]. Van der Waals and Platteeuw developed the first thermodynamic model to predict hydrate equilibrium [6], which was later generalized by Parrish and Prausnitz [3] to form the basis of most models to date. Lee and Holder [7] observed through experimental studies that cavity distortion occurred due to changes in guest molecule size and proposed a unique reference chemical potential for each hydrate former, and later Lee and his colleague calculated reference chemical potential for various gas hydrates using a molecular dynamic simulation method [10].

This study aims to calculate the reference chemical potential of the theoretical empty cavity and especially the effect of temperature on enthalpy changes of structure II gas hydrates, using a molecular dynamics (MD) simulation method, with the Lee-Holder distortion model as the basis. All simulations employed the TIP4P water model and were performed in the NVT (constant number of molecules, volume and temperature) ensemble along with the Gaussian thermostat for temperature regulation, while the Link cell and Ewald sum techniques were incorporated to calculate the short and long range forces, respectively. Apart from determining the reference chemical potential, MD simulations were also conducted to determine the effect of varying temperature on the hydrate unit cell size.

THEORETICAL BACKGROUND

The coexistence of the hydrate phase with liquid and vapor phases is a prerequisite for the stability of clathrates whose equilibrium

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calculations are governed by the Gibbs Phase rule. At equilibrium, the chemical potential of water in the hydrate phase μ_w^H is the same as that in liquid state μ_w^W [4]. Considering chemical potential of the theoretical empty hydrate μ_β as the reference state, the difference is given as [4,6-7,9]

$$\begin{aligned}\Delta\mu_w^H &= \mu_\beta^W - \mu_w^H \\ \Delta\mu_w^W &= \mu_\beta^W - \mu_w^W\end{aligned}\quad (1)$$

For stable existence of the hydrate structure, (i.e., at equilibrium) the above two equations are equal:

$$\Delta\mu_w^H = \Delta\mu_w^W \quad (2)$$

van der Waals and Platteeuw were the first to draw a similarity between gas hydrate formation and Langmuir's adsorption theory, where the Langmuir constant for each being a function of temperature, cavity occupancy and participating molecules. In case of clathrates, it is given by C_{ij} where i is a cavity in hydrate lattice occupied by j type guest molecule. The fractional occupancy, θ_j , for single guest occupancy in each cavity is given by [11]

$$\theta_j = C_{ij} f_i / \left(1 + \sum_{i=1}^N C_{ij} f_i \right) \quad (3)$$

where C_{ij} is the Langmuir constant of component i in j cavity ($j=1$ for a small cavity and $j=2$ for a large cavity in structure I and structure II gas hydrate) and f_i is the fugacity of component i in gas hydrate.

Assuming spherical symmetry, the Langmuir adsorption coefficient is given by [4,12]

$$C_{ij} = 4\pi/kT \int_0^R \exp\left(-\frac{W(r)}{kT}\right) r^2 dr \quad (4)$$

where $W(r)$ is the spherical cavity cell potential and is calculated using the Kihara potential model. Based on this, they proposed a thermodynamic model to predict gas hydrate equilibria, however neglecting the effect that the size of guest molecule may have on the cavity. The chemical potential of gas hydrate by van der Waals and Platteeuw would be expressed as,

$$\Delta\mu_w^H = \mu_w^\beta - \mu_w^H = -kT \sum_i v_i \ln\left(1 - \sum_j \theta_j\right) \quad (5)$$

Parrish and Prausnitz generalized the van der Waals and Platteeuw model by suggesting a temperature and pressure dependence for the chemical potential difference; however, it did not account for the misalignment of the hydrate lattice due to the size of guest molecules [3,4,6]. Lee and Holder [7-9] were the first to propose, through the distortion model, the effect of guest molecule size on the hydrate cavity and the necessity of unique reference properties for each guest molecule. The model, which accounted for the effect of temperature, pressure and composition to calculate the chemical potential difference, is given by

$$\frac{\Delta\mu_w^W}{RT} = \frac{\Delta\mu_w^o}{RT_o} + \int_{T_o}^T \frac{\Delta h_w}{RT^2} dT + \int_{P_o}^P \frac{\Delta V_w}{RT} dP - \ln \gamma_w x_w \quad (6)$$

In the above equation, the first term on the right is the reference chemical potential difference between water and theoretical empty cavity at T_o , the second term accounts for the temperature depen-

dence of hydrate chemical potential at zero pressure, the next term corrects the pressure to its equilibrium value, while the last term provides a correction for water rich solution [4,7-9].

The temperature dependent enthalpy, in the above equation, is given as

$$\Delta h_w = \Delta h_w^o + \int_{T_o}^{T_f} \Delta C_{P_w} dT \quad (7)$$

where Δh_w^o is the reference enthalpy difference between water and theoretical empty cavity. The enthalpy changes due to temperature can be obtained as a function of specific heat capacity and temperature.

$$\Delta C_{P_w} = \Delta C_{P_w}^o + b(T - T_o) \quad (8)$$

where b is an empirical constant fitted to experimental data and $\Delta C_{P_w}^o$ is the reference specific heat capacity.

Interaction between adjacent guest molecules stretches the hydrogen bonds between water molecules to minimize the total energy, resulting in cavity distortion. Hence, hydrate equilibria became more, the subject of interaction between hydrate lattice and guest molecules. With the assumption that the cavity would be distorted to minimize the total Gibbs energy, the chemical potential difference between water and theoretical empty cavity ($\Delta\mu_w^o$), the enthalpy difference (Δh_w^o), and the reference specific heat capacity ($\Delta C_{P_w}^o$) would have different values for each gas hydrate, while the prior models would have the same values for all gas hydrates. In the present study, we follow the Lee-Holder model [7], which considers a unique value of the reference chemical potential for each hydrate former.

MOLECULAR DYNAMICS SIMULATION

Computer simulations act as a bridge between experimental results and theoretical calculations. Molecular dynamics is a computer simulation technique which describes the dynamic behavior of a set of interacting particles by integrating Newton's equations of motion and generates particle trajectories from which time averaged macroscopic properties like diffusivity, viscosity and thermal conductivity can be calculated [13].

In the present study, we used MOLLY® [14] for performing molecular dynamics simulation of structure II gas hydrates using the NVT ensemble, and values were adjusted to optimize the unit cell volume of gas hydrate containing guest molecules. The program can handle any mixture of polyatomic molecules, of any size within a rigid frame structure. It uses the 'link-cell' method for calculating short-range forces and the Ewald sum technique for calculating long range electrostatic forces [15]. The Gaussian thermostat was employed to maintain a constant temperature that was between 140 K and 290 K. Interactions between the guest gas molecule and water molecules were represented by the Lennard-Jones 12-6 pair potential and the Lorentz-Berthelot mixing rule approximated the interactions between unlike molecules [16]. The MD simulations of structure II clathrate hydrates were performed with the skew start and lattice start methods in MOLLY® [10]. The quaternion data was obtained using the empty hydrate skew-start in MOLLY. Jorgensen's TIP4P model consisting of one O-site, two H-sites and

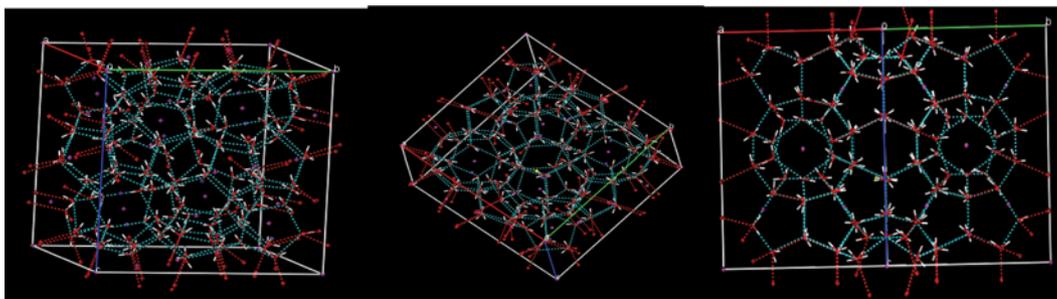


Fig. 1. Stabilized Krypton hydrate unit cell.

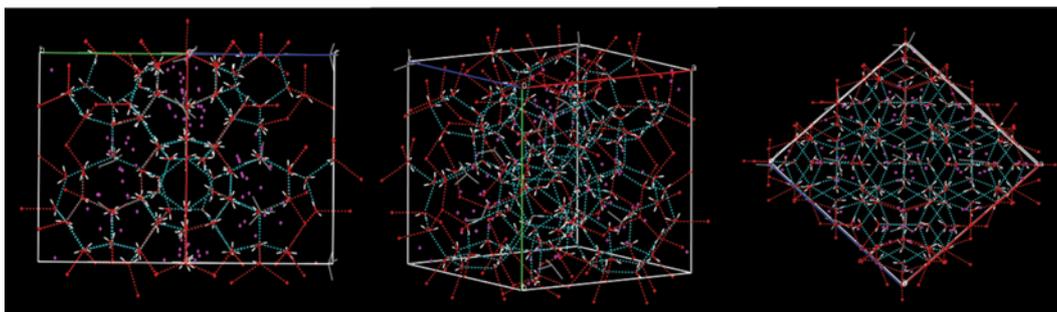


Fig. 2. Stabilized isobutane hydrate unit cell.

a hypothetical M-site was used to describe water-water interactions, with partial charges assigned to the H and M-sites [17]. The empty hydrate structure is highly unstable and hence, a large number of simulations were performed to determine the exact step size for near equilibrium conditions.

The simulation of structure II clathrate hydrates, with the cavities occupied by the guest molecule, was performed using the data from the initial stable configuration. Various hydrate formers like krypton, argon, propane, nitrogen were considered in this work. For all the hydrate formers, interactions between pairs of sites within a cutoff radius of 8.5125 Å were included. Unit cell dimensions of gas hydrate containing various guest molecules were determined after the structure was stabilized. The stabilized unit cell size at the ice point temperature varies with different guest molecules, which implied each guest molecule distorts the cavity structure of gas hydrate [7-10,18]. The reference chemical potential difference is defined as the chemical potential difference between water and the theoretical empty cavity at ice point (273.15 K) that can be determined from the chemical potential difference between hydrate and theoretical empty cavity. In this research to determine the unit cell size change according to temperature, the gas hydrate structure with guest molecules was stabilized not only at the ice point but also over and below the ice points, and from the unit cell dimension changes to the temperature, the thermal expansion of gas hydrate can be determined.

RESULTS AND DISCUSSION

MD simulation techniques are used to establish equilibrium conditions for various clathrate hydrates and determine their reference enthalpies and thermal expansivity. The structure II hydrate

formers were considered for this study including argon, krypton, propane, cyclopropane and isobutane. Structures for krypton and isobutane in the stabilized hydrate regions are shown in Fig. 1 and Fig. 2. The structure II hydrate contains 16 small and 8 large cavities. In the figures, the lines are hydrogen bonds and the guest molecules are located at the center of cavities. Both hydrates have the same crystal structures, but isobutane hydrate has a larger unit cell size than krypton hydrate at the same temperature since the molecular size of isobutane is larger than that of krypton. Generally, larger guest gas molecules would expand their unit cell size larger to stabilize the crystal structure.

Representative MD simulation results to make hydrate structure stable are shown in Fig. 3. In the figure, total energy as well as pressure decreases gradually and smoothly with an increase in simulation time, and after 75-85 femto seconds (fs) the total energy was stabilized and reached the equilibrium state where the total energy became minimum. Different equilibrium pressures and

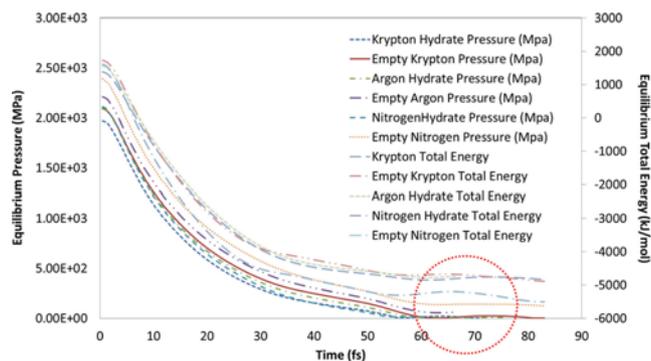


Fig. 3. Equilibrium plot for Nitrogen, Krypton and Argon hydrates.

minimum energies at the equilibrium condition can be obtained for each gas hydrate. During the simulation, the equilibrium pressure was determined after the total energy had stabilized at a given unit cell size of each gas hydrate. To determine the unit cell size of each gas hydrate, equilibrium pressures were calculated with MD simulations by changing the unit cell size, and the unit cell size which gives the same equilibrium pressure as the experimental equilibrium pressure was used as the distorted unit size of gas hydrate. While changing the unit cell size, we used the assumption of isentropic distortion of the unit cell. The detailed procedure to get the reference properties of gas hydrates is explained in the other article [10].

To get the thermal expansion of gas hydrate at temperature change, MD simulations were conducted at various temperatures, and each unit cell size at each temperature was obtained. Calculation results are summarized in Fig. 4. In the figure, the unit cell size increased almost linearly with respect to temperature since there is generally no second-order distortion in single component gas hydrates even if mixture gas hydrates can have second-order distortion that makes correlation between unit cell size and temperature more complicated [9,18]. This correlation is expressed for

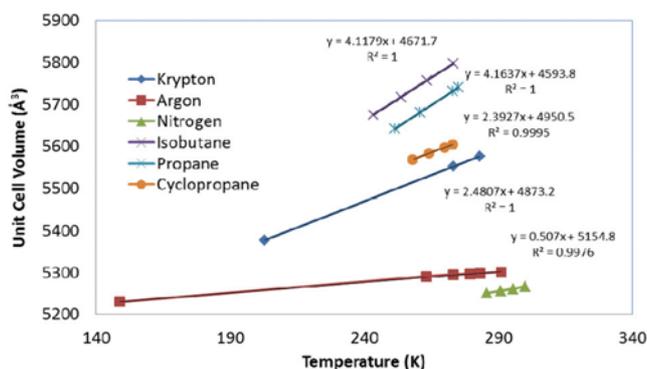


Fig. 4. Thermal expansion of hydrate unit cell.

Table 1. Empirical parameters for thermal expansion

Guest	Diameter (Å)	A	B
Argon	3.8	0.570	5154.8
Krypton	4.0	2.4807	4873.2
Cyclopropane	5.8	2.3927	4950.5
Propane	6.28	4.1634	4593.2
Isobutane	6.5	4.1179	4671.7

Table 2. Comparison of the Δh_w^0 values calculated by the LHD model and calculated by MD simulations

Guest	Δh_w^0 (MD simulation)	Δh_w^0 (LHD)
Argon	1075.33	1038.07
Krypton	795.81	820.42
Nitrogen	901	937
Cyclopropane	1315.38	1254
Isobutane	1918.18	1972
Propane	1549.09	1479.7

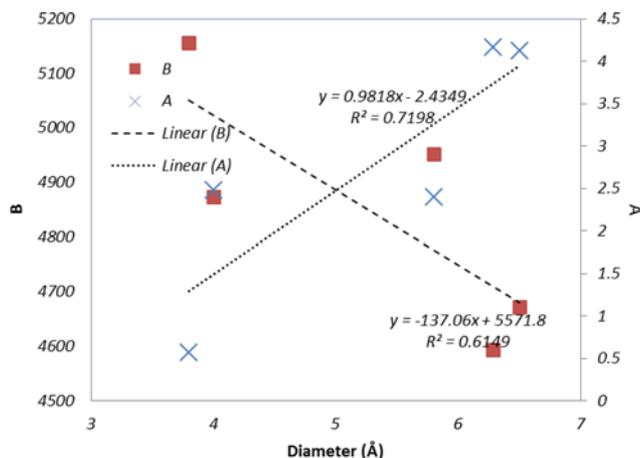


Fig. 5. Constants A and B depending on the size of guest molecules.

single component hydrates as a linear function in Eq. (9).

$$V(\text{unit cell volume, } \text{Å}^3) = A + B \times T \text{ (Kelvin)} \quad (200 \text{ K} < T < 280 \text{ K}) \quad (9)$$

Here, A and B are empirical parameters obtained from MD simulations and summarized in Table 1. The gas hydrate structure that contains larger guest molecules has a relatively larger volume at a given temperature and those expand at higher temperatures. Dependency of the parameters on the guest size is shown on Fig. 5, where, parameter A represents the initial unit cell size that increases with the size of the guest molecule. Since the unit cell size of gas hydrate in equilibrium calculations should be determined at 273.15 K, 'A' would be an adjustable parameter to make the unit cell size of each gas hydrate to the simulated value at the reference condition. B represents the temperature dependency on the unit cell size that decreases at size of the guest molecule. It can be explained that the changes of the unit cell size of the gas hydrate containing larger guest molecules would be small at temperature changes since the cavities are already expanded and that gives less flexibility of the structure.

Reference chemical potential differences were then obtained for the clathrates at 273.15 K and 0 kPa; the values obtained were plot-

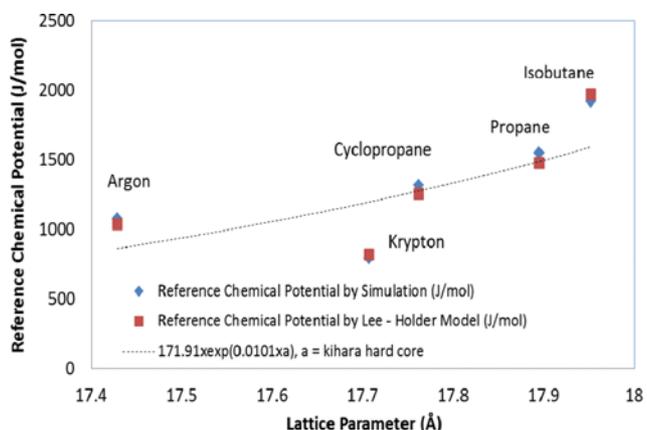


Fig. 6. Reference chemical potential differences as a function of lattice parameter for propane, cyclopropane and isobutane hydrates.

ted against unit cell lattice parameters and compared with the empirical calculation results by the Lee-Holder model [7] as shown in Fig. 6. The average deviation between two different calculations was 4.7% and the maximum deviation was 8.7% for propane. Sloan and Koh [11] compiled some experimental data for the lattice parameter of propane, and the lattice parameter is smaller than 17.3 angstrom at a temperature range of 0-250 K, but our calculations result showed around 17.9 at the reference condition of 273.15 K and 0 bar. The temperature difference leads to the different lattice parameters. Reference enthalpy differences were also calculated and summarized in Fig. 7. For reference enthalpy, the average deviation was 3.53% and the maximum deviation was 5.015% for Krypton. No noticeable trend of the reference enthalpy differences has been found in this study.

In Fig. 7, Argon hydrate and krypton hydrate have relatively larger reference enthalpy values at small unit cell sizes. It seems that both small and large cavities can capture gas molecules for argon

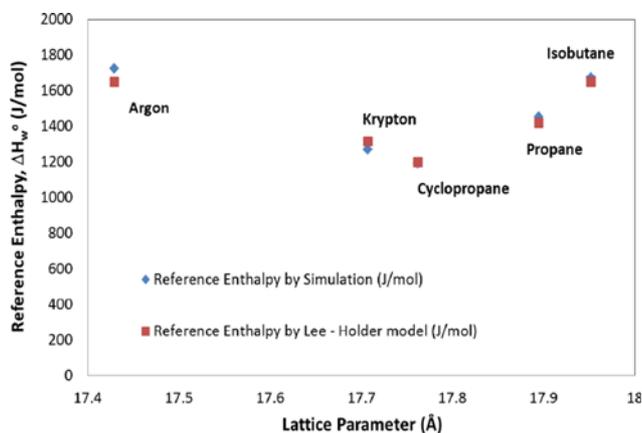


Fig. 7. Reference enthalpies.

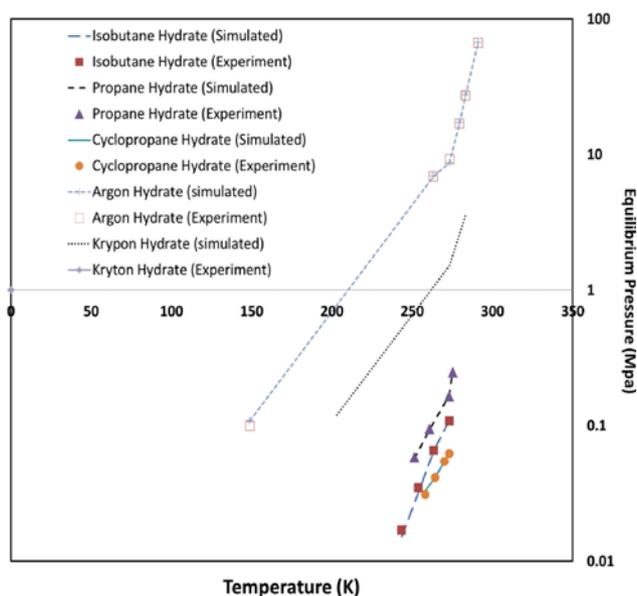


Fig. 8. Equilibrium calculation of gas hydrate using reference enthalpies and thermal expansivity.

or krypton hydrates, which would make these hydrates have larger reference enthalpies at relatively small distortions. Equilibrium conditions for various gas hydrates using the reference chemical potentials, reference enthalpies, and thermal expansivities by MD simulations were calculated and listed in Fig. 8. As shown, a very accurate prediction for the equilibrium conditions of single component gas hydrate was obtained and the average error was around 4% compared with the experimental values [7].

CONCLUSION

The growing importance of clathrate hydrates as a source of energy and energy storage medium has provided an impetus for their phase equilibrium study. We determined unit cell size, reference chemical potential, and reference enthalpy and calculated the equilibrium conditions for various structure II hydrate formers by performing MD simulations using MOLDY. From the equilibrium plots, it was concluded that all the guest molecules stabilized in a zone of 75-85 fs. Apart from determining the equilibrium region for guests, the simulation results also illustrated thermal expansion of hydrate unit cells. Assumptions in the Lee-Holder distortion model were applied to determine unique reference properties for each guest molecule. Furthermore, the reference enthalpy and chemical potential values obtained were used to evaluate specific heats for each hydrate former considered in this study.

ACKNOWLEDGEMENT

This research was supported by the research program of Dongguk University (Seoul, Korea) and also supported by the project titled "Development of Key technology in seawater desalination using gas hydrate process" funded by Ministry of Oceans and Fishery Korea.

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