ORIGINAL ARTICLE

# The influence of temperature, pressure, salinity and capillary force on the formation of methane hydrate

## Zhenhao Duan [a],*, Ding Li [a], Yali Chen [b], Rui Sun [c]

[a] *Key Laboratory of the Earth's Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China*
[b] *School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China*
[c] *Northwest University, Xi'an 710069, China*

**Abstract**    We present here a thermodynamic model for predicting multi-phase equilibrium of methane hydrate liquid and vapor phases under conditions of different temperature, pressure, salinity and pore sizes. The model is based on the 1959 van der Waals−Platteeuw model, angle-dependent *ab initio* intermolecular potentials, the DMW-92 equation of state and Pitzer theory. Comparison with all available experimental data shows that this model can accurately predict the effects of temperature, pressure, salinity and capillary radius on the formation and dissociation of methane hydrate. Online calculations of the $p-T$ conditions for the formation of methane hydrate at given salinities and pore sizes of sediments are available on: www.geochem-model.org/models.htm.

* Corresponding author.
   E-mail address: duanzhenhao@yahoo.com (Z. Duan).

## 1. Introduction

Gas hydrate (or clathrate hydrate) is composed of cages bonded by water molecules and guest molecules encapsulated in the cages through van der Waals forces between the guest and water molecules. Only when the cage space and the size of guest molecules match each other can a stable clathrate hydrate be formed. At present, gas hydrate is discovered in oil and gas pipelines, marine sediments, permafrost (Sloan, 1998), comets and some foreign planets (Lunine and Stevenson, 1987). Presently known natural gas reserve stored in gas hydrate (mainly methane hydrate) is considered to be huge. 1 m$^3$ of methane hydrate can release 164 m$^3$ of methane gas. Thus, methane hydrate is considered to be highly compressed natural gas and an obvious potential clean energy source and a substitute for fossil fuels. In addition, release of methane gas from oceanic and permafrost hydrates into the atmosphere could have an important impact on global warming

(Dickens, 2003). Xu and Germanovich (2006) have proposed that gas hydrate melting can trigger submarine landslides.

Methane hydrate under high pressure and low temperature is stable. Fig. 1 is the phase diagram of the CH₄−H₂O binary system. Q is the quadruple invariant point, where methane hydrate (H), ice (I), water-rich liquids (L) and CH₄-rich gas (V) coexist. Line AQB shows p−T conditions when H−I−V and H−L−V reach equilibrium and it also indicates the boundary on which methane hydrate is stable. Based on phase equilibrium conditions, the region on both sides of the line AQB is the two-phase region, where in the region above AQB methane hydrate is stable and below AQB methane-rich gas and liquid water or ice coexist.

Since van der Waals and Platteeuw (1959), a number of scholars have proposed thermodynamic models to calculate the equilibrium of gas hydrate. However, previous work is mostly on the gas hydrate three-phase equilibrium of bulk systems, including Parrish and Prausnitz (1972), Ng and Robinson (1976), Englezos and Bishnoi (1988), Tohidi et al. (1995), Chen and Guo (1998), Ballard and Sloan (2002), and Lee and Holder (2002). Clennell et al. (1999) and Henry et al. (1999) designed a thermodynamic model to predict the three-phase equilibrium of methane hydrate in marine sediments by using the Gibbs−Thomas equation calculating the capillary effect caused by small pores. Later, Klauda and Sandler (2001) proposed a model predicting the distribution of methane hydrate in marine sediments, but parameters in these models are not accurate enough (Llamedo et al., 2004). These models overestimate the inhibitory effect of capillary force on the H−L−V equilibrium.

Most published models predict the conditions of methane hydrate formation using the Kihara potential model, where parameters are derived from the experimental data of hydrate phase equilibrium and cage occupancy. While these models after assignment fit very well with experimental data, their predictive power is poor. For instance, models by Parrish and Prausnitz (1972) and the CSMHYD model by Sloan (1998) predicting the hydrate phase equilibrium only apply when pressure is lower than (400−500) × 10⁵ Pa. In addition, the Kihara potential energy surface obtained by the experimental data doesn't agree with that of Tee et al. (1966) whose calculations used the second virial coefficient and viscosity data. Hence, the Kihara potential model cannot accurately describe the interactions between water molecules and guest molecules. Potential parameters obtained simply
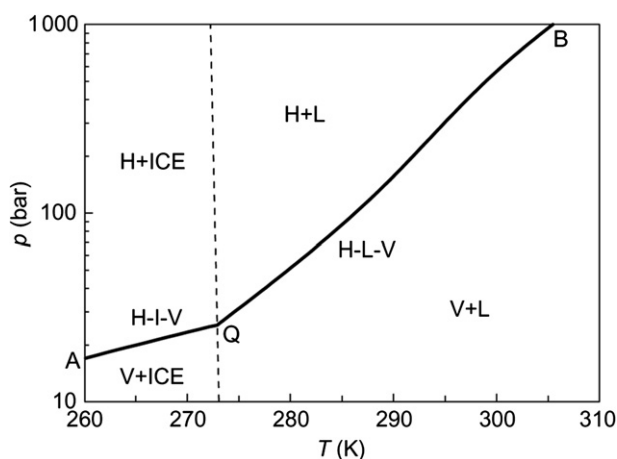
by fitting macroscopic system experimental data cannot accurately reflect the potentials of microscopic molecular interactions. Therefore, in this study we use the atomic site−site potentials model. This model takes into account the molecular interaction's dependence on the angle, and its parameters are calculated using the *ab initio* method instead of being derived from macroscopic experimental data.

The goal of this study is to build an accurate H−L−V three-phase equilibrium model to predict the effect of temperature, pressure, salinity and capillary force on the formation and dissociation of methane hydrate based on the van der Waals and Platteeuw (1959) model, *ab initio* intermolecular potentials, equation of state by Duan et al. (1992b) and Pitzer (1991) theory. Among the models, the basic hydrate model by van der Waals and Platteeuw (1959) is used to describe the chemical potential of the hydrate phase; the *ab initio* intermolecular potentials is used to calculate the Langmuir constant; and Duan et al.'s (1992b) equation of state is applied to calculate the fugacity of methane gas.

## 2. Thermodynamic model of hydrate

### 2.1. Methane hydrate formation temperature and pressure in pure water

When the methane hydrate phase is in equilibrium with the liquid water or ice phase, the chemical potentials of water in the former ($\mu_w^H$) and in the later ($\mu_w^L$) are the same, namely

$$\mu_w^H = \mu_w^L \tag{1}$$

If we make the chemical potential of empty hydrate lattice a reference state at the same temperature and pressure, then

$$\Delta\mu_w^H = \mu_w^\beta - \mu_w^H = \mu_w^\beta - \mu_w^L = \Delta\mu_w^L \tag{2}$$

Therefore, theoretical models that predict formation conditions of gas hydrate consist of two parts: one for gas hydrate phase and the other for pure water phase (liquid water or ice). The former is usually based on van der Waals and Platteeuw (1959) adsorption isotherm theory and the latter is based on Holder et al.'s (1980) expressions.

Based on classical statistic mechanics and Langmuir adsorption isotherm theory, van der Waals and Platteeuw (1959) derived the expression for the difference of chemical potentials between empty hydrate phase and filled hydrate phase:

$$\Delta\mu_w^H(T,p) = -RT \sum_{i=1}^{2} v_i \ln\left(1 - \sum_{j=1}^{N_C} \theta_{ij}\right) \tag{3}$$

where $v_i$ is the number of $i$-type cages per water molecule (in sI-type hydrate, $v_i = 1/23$ for small cages and $v_i = 3/23$ for big cages); $N_C$ is the number of components that can form hydrate; $\theta_{ij}$ is the fractional occupancy of small cavities with $j$-type guest molecules whose expression is:

$$\theta_{ij} = \frac{C_{ij} f_j}{1 + \sum_{j=1}^{N_C} C_{ij} f_j} \tag{4}$$

where $f_j$ is the fugacity of guest molecules in each phase; $C_{ij}$ is the Langmuir constant of guest molecule $j$ in $i$-type cages, which is usually calculated by intermolecular potential functions. The definition of $C_{ij}$ is:



**Figure 1**    p−T phase diagram of the CH₄−H₂O binary system at low temperatures.