

THERMODYNAMICAL INVESTIGATION OF HYDRATE FORMATION IN NATURAL GAS

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***Abstract.** In the last fifty years, many researchers have been working on general thermodynamical equilibrium problems, including multicomponent isothermal flash applied to oil recovery, complex mixtures separation dynamics, and critical conditions equilibria. Most of these works have been focused on many different subjects of the vapor-liquid equilibrium of complex mixtures, such as physical models, equations of state, combining and mixing rules and optimization methods. In order to evaluate the equilibrium behavior, it is necessary to calculate the chemical's composition of each phase under equilibrium condition. Indeed, several models were introduced based on the equality of the chemical potential of the species of each phase. Such models can be redefined and thus the molar Gibbs energy for a given temperature and pressure must be minimum. In complex system, as those involving hydrates formation, the molar Gibbs energy is a multivariate function, and thus the minimum of such function may involve the search of a global extremum. In this work, a new formulation is introduced that aims to find out the composition of the equilibrium during the hydrate formation through a cubic equation of state using an stochastic algorithm. The results from the present formulation are favourably compared with both numerical results from other formulations and experimental data.*

Keywords: Natural Gas, Hydrate, Stochastic Algorithm, Cubic Equation of State

1. INTRODUCTION

Natural gas (NG) is a gaseous fossil fuel consisting mainly of methane and significant amount of light hydrocarbons (ethane, propane and butane), carbon dioxide, nitrogen, hydrogen and water (Carroll, 2003). It may be found in oil and gas fields and coal beds. Technologies based on NG are used in a wide range of chemical, and energy generation processes with a budget of billion dollars annum (Sloan, 1998). The contaminants are also used, but they have a lesser aggregate value. Water, in particular, must be removed to prevent the hydrate formation which may increase the costs of production and refining and drop the efficiency in processing and transporting the NG (Sun & Chen, 2006).

Hydrates are crystalline solid, similar to the ice, composites of not stoichiometric hydrocarbons (HC) (C₁-C₅) and water (see Sloan, 1998). They are denser than typical fluid HC and the gas molecules they contain are compressed in a complex network. Propane and n-butane may form unstable hydrates whereas pentane hydrates are usually inhibited by methanol, ethanol, monoethyleneglycol (MEG) and diethyleneglycol (DEG). Hydrates of alkanes in the crystalline form may appear at

very mild industrial conditions of temperature and pressure (e.g. 21°C and 300E+5 Pa).

Two conditions are essential in the hydrate formation, (a) temperature and pressure (b) presence of hydrocarbons and H₂O. Water one of the components of hydrates. For having its point of anomalous bubble (high enthalpy of vaporization with regard to other polar molecules), it has lesser density in its solid form. The crystal structure may occupy a large space in the liquid phase and if mixed with a gas, it may form a precipitant mixture, i.e., hydrates. The free water facilitates the hydrate formation (Carroll, 2003).

Carroll (2003) classified the hydrates based on the crystallographic structure, i.e., the arrangement of water molecules in the crystal: (a) type I: there are 46 water molecules forming small (pentagonal dodecahedron shape) and large (tetraikaidecahedron shape) cages (see also Sloan, 1998, for further details). Its composition is: CH₄, ethane, CO₂, H₂S; (b) type II: its structure is more complex than type I with 136 molecules of water molecules surrounding nitrogen, propane and isobutane. They form cages with a pentagonal dodecahedron shape and hexakaidecahedron shape cage; (c) type H - they are rarer and consists of 34 molecules of water in three types of cages and require two guest gases to become stable.

In this work, the formation of types I and II hydrates are investigated through the study of the equilibrium of the aqueous and hydrate phases in a multi component systems. Individual equations of state are used for each guest molecules and water with a suitable mixing rule. In addition, the authors considered that the enclathration rate of guest molecules is similar to the rate of desorption. The equilibrium conditions, at constant temperature and pressure, are achieved by minimizing the free Gibbs energy. Thus, the equilibrium calculation is designed as a problem of global optimization of the nonlinear (free Gibbs energy) and multi variable function (Henderson *et al.*, 2001).

2. THE THERMODYNAMICAL MODEL

Hydrates formation occurs at low temperature and high pressures conditions (Ballard & Sloan, 2002). The thermodynamic formulation used in this work is presented here. In order to reach the equilibrium state in a closed system, three conditions must be fulfilled (Callen, 1985): (a) temperature (T^k) and (b) pressure must be constant in all the phases (P^k) and (c) the fugacities (f_i^k) of each component must be constant in all phases.

In a system with c components and π phases, the mass conservation requires that:

$$\sum_{k=1}^{\pi} \alpha^k x_i^k = z_i \quad i = 1, c \quad (1)$$

with the following constraints

$$\sum_{k=1}^{\pi} \alpha^k = 1 \quad (2)$$

and

$$\sum_{i=1}^c x_i^k = 1 \quad k = 1, \pi \quad (3)$$

where α is the molar phase fraction, x_i^k is the mole fraction of component i in phase k and z is the global composition. Introducing a reference phase R , the mass balance, Eqn. 1 may be written as

$$\left[\alpha^R + \sum_{k=1, k \neq R}^{\pi} \alpha^k \frac{x_i^k}{x_i^R} \right] x_i^R = z_i \quad (4)$$

The constant fugacity in all phases for a given component may be expressed as

$$\frac{f_i^R}{f_i^k} = \frac{x_i^R \phi_i^R P}{x_i^k \phi_i^k P} = 1 \quad i = 1, c \quad k = 1, \pi \quad (5)$$

where ϕ is the fugacity coefficient. Equation 5 may be rewritten as, follows by defining \mathcal{K}_i^k

$$\mathcal{K}_i^k = \frac{\phi_i^R}{\phi_i^k} = \frac{x_i^k}{x_i^R} \quad i = 1, c \quad k = 1, \pi \quad (6)$$

This expression is satisfied only if all phases are present in the equilibrium. In the calculation of hydrates formation, Eqn. 6 must be redesigned in order to allow the calculation for all phases, present or not. Considering that

$$\frac{f_i^R}{f_i^k} \begin{cases} = 1 & \text{if phase } k \text{ is present} \\ < 1 & \text{if phase } k \text{ is not present} \end{cases} \quad (7)$$

Multiplying the mole fraction ratio, \mathcal{K}_i^k (Eqn. 6), by the fugacity ratio (Eqn. 7) leads to

$$\mathcal{K}_i^k = \frac{x_i^k}{x_i^R} \exp \left[- \ln \frac{f_i^k}{f_i^R} \right] \quad (8)$$

Defining θ^k as the stability parameter of phase k

$$\theta^k = \ln \frac{f_i^k}{f_i^R} \quad (9)$$

Equation 8 may be rewritten as (see Sloan, 1998)

$$\frac{x_i^k}{x_i^R} = \mathcal{K}_i^k e^{\theta^k} \quad (10)$$

Equation 10 is valid for all phases regardless their presence in the equilibrium.

3. THE FREE GIBBS ENERGY MINIMIZATION

As expressed by the *Gibbs potential minimum principle* (Callen, 1985), ‘the equilibrium value of any unconstrained internal parameter in a system minimizes the Gibbs potential at constant temperature and pressure’. Therefore, the equilibrium state can be written as an optimization problem, $\Delta G \rightarrow \min$ (Gomes *et al.*, 2001) Equation 10 describes the composition in the equilibrium regardless the presence of any phase. Replacing the mole fraction ratio from Eqn. 10 in the mass balance (Eqn. 4) leads to

$$\left[\alpha^R + \sum_{k=1, k \neq R}^{\pi} \alpha^k \mathcal{K}_i^k e^{\theta^k} \right] x_i^R = z_i \quad (11)$$

with the mole fraction constraints defined in Eqn. 2 ((assuming that $\mathcal{K}_i^R = 1$ and $\theta^R = 0$))

$$x_i^k = \frac{z_i \mathcal{K}_i^k e^{\theta^k}}{1 + \sum_{j=1, j \neq R}^{\pi} \alpha^j (\mathcal{K}_i^j e^{\theta^j} - 1)} \quad i = 1, c \quad k = 1, \pi \quad (12)$$

From the mole fraction constraint (Eqn. 3), the objective function, Φ^k , is obtained

$$\Phi^k = \sum_{i=1}^c \frac{z_i (\mathcal{K}_i^k e^{\theta^k} - 1)}{1 + \sum_{j=1, j \neq R}^c \alpha^j (\mathcal{K}_i^j e^{\theta^j} - 1)} = 0 \quad k = 1, \pi \quad (13)$$

Ballard & Sloan (2002) (see also Sloan, 1998) showed that by defining the mole fraction ratio, as defined by Eqn. 10, Φ^k is equivalent to the free Gibbs energy. In this work, the fugacity model in the clathrate is based on the Van der Waals & Platteeuw (1959) approach (see Chen & Guo, 1996; Ballard & Sloan, 2002; Inerbaev *et al.*, 2006; Sun & Chen, 2006), in which the guest species' fugacity is calculated from the Patel & Teja (1982) EOS. This hybrid model is based on fugacity of the guest molecules (i.e., the desorption rate) in the gas phase and the activity of water molecules in the aqueous phase.

4. RESULTS

The results shown in this section are preliminary and need, thus, to be fully benchmarked. Simple methane and ethane solutions were chosen in a narrow range of pressure and temperature conditions. Pressure *against* temperature of methane and ethane hydrate formation are shown in Fig. 1. At lower pressures, the results obtained by the model described in this work, matches a few experimental data from the literature. However, at larger pressure, discrepancies occurred, suggesting that further fitting in the equations of state parameters should be performed (e.g., stoichiometric hydrate parameters, Langmuir desorption rate constant, and others). The composition of the guest molecules at the aqueous phase *against* temperature at constant pressure (300 MPa) is shown at Fig. 2.

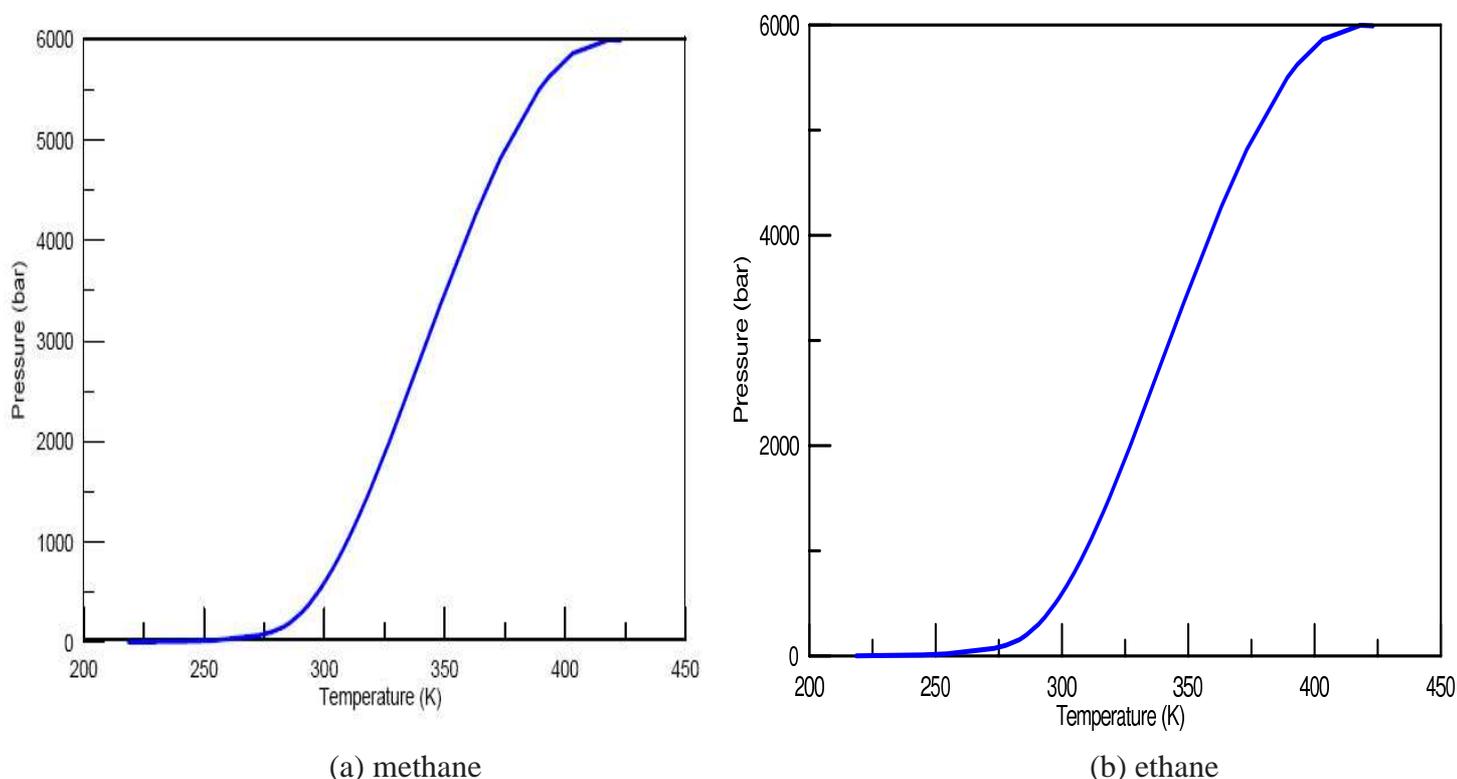


Figure 1. Pressure \times temperature at constant feeding composition of (a) methane and (b) ethane.

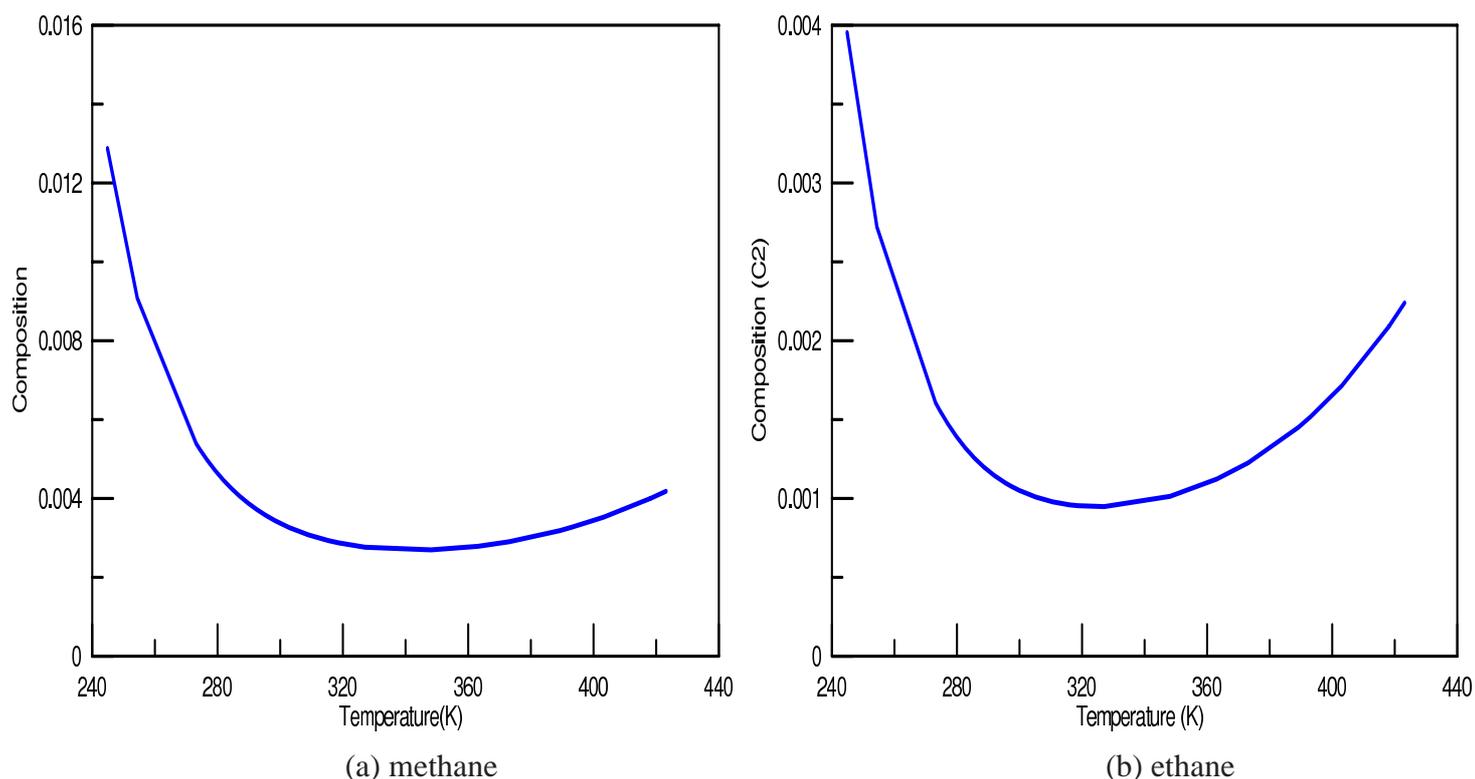


Figure 2. Temperature \times guest molecules molar composition at constant pressure (300 bars): (a) methane and (b) ethane.

5. CONCLUSION

This work reports the first part of the research project to model the hydrate formation in natural gas. The thermodynamical formulation used here takes into account the kinetics mechanisms of hydrate formation, non-stoichiometric properties of hydrates and clustering stability (i.e., filling of cavities with guest molecules). Using individuals equations of state for each guest molecules and water may allow the accurate prediction of the thermodynamical behaviour of each specie, however in order to avoid discontinuities in the equilibrium conditions, consistent and adaptive fitting parameters for all equations of state and mixing rules (when appropriate) are necessary. The general thermodynamical model is shown in this work and the full model will be presented soon. The results shown here at relatively low pressure conditions matches well with experimental data, however at larger pressures, discrepancies occurred, possibly due to fitting parameters.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

- Ballard, A.L., Sloan Jr., E.D., 2002, "The Next Generation of Hydrate Prediction: An Overview". *Supramolecular Chemistry*, Vol. 2, pp. 385-392.
- Callen, H.B., 1985, "Thermodynamics and an introduction to thermostatics", Wiley, New York, USA.
- Carroll, J., 2003, "Natural Gas Hydrates: a Guide for Engineers", Gulf Professional Publishing, London, UK.

- Chen, G.J., Guo, T.M., 1996, "Thermodynamic modelling of hydrate formation based on new concepts", *Fluid Phase Equilibria*, Vol. 122, pp. 43-65.
- Corana, A., Marchesi, M., Marchesi, C., Ridella, S., 1987, "Minimizing Multimodal Functions of Continuous variables with the Simulated Annealing Algorithm", *ACM Transactions on Mathematical Software*, Vol. 1, pp. 262-280.
- Jager, M.D., Ballard, A.L., Sloan Jr., E.D., "Comparison between experimental data and aqueous-phase fugacity model for hydrate prediction", *Fluid Phase Equilibria* 232 (2005) 25-36
- Gomes, J.L.M.A., Henderson, L.N., Rocha, M.C.G., 2001, "Modelling the Vapor-Liquid Equilibrium of Polymer Solutions Using a Cubic Equation of State", *Macromolecular Theory and Simulations*, Vol. 10, pp. 816-826.
- Henderson, L.N., de Oliveira Jr., J.R., Souto, H.P.A., Marques, R.P., 2001, "Modelling and Analysis of the Isothermal Flash Problem and its Calculation with the Simulated Annealing Algorithm", *Ind. Eng. Chem.*, Vol. 40, pp. 6028-6035.
- Henderson, L.N., Freitas, L., Platt, G.M., 2004, "Prediction of critical points: A new methodology using global optimization", *AIChE Journal*, Vol. 50, pp. 1300-1314.
- Inerbaev, T.M., Belosludov, V.R., Belosludov, R.V., Sluiter, M., Kawazoe, Y., 2006, "Dynamics and equation of state of hydrogen clathrate hydrate as a function of cage occupation", *Computational Materials Science*, Vol. 36, pp. 229-233.
- Patel, N., Teja, A.S., 1982, "A New Cubic Equation of State for Fluids and Fluid Mixture", *Chemical Engineering Science*, Vol. 37, pp. 463-473.
- Sloan Jr., E.D., 1998, "Clathrate Hydrates of Natural Gases", M. Dekker, New York, USA.
- Sun, C.Y., Chen, G.J., 2006, "Modeling the hydrate formation condition for sour gas and mixtures", *Chemical Engineering Science*, Vol. 60, pp. 4879-4885.
- van der Waals, J.H. & Platteeuw, J.C., 1959, "Clathrate solutions", *Adv. Chem. Phys.*, Vol. 2, pp. 1-57.

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