Comparison of Computational Methods for Hydrate Phase Equilibria

Yong Soo Kim

Thermodynamic Lab.

Chemical Engineering, Korea Univ.

Introduction

- Application of gas hydrates
  - The methods to harvest the huge amounts of methane hydrate are being developed.
  - It is possible to use hydrates as a sequestering media for carbon dioxide at the bottom of the ocean.

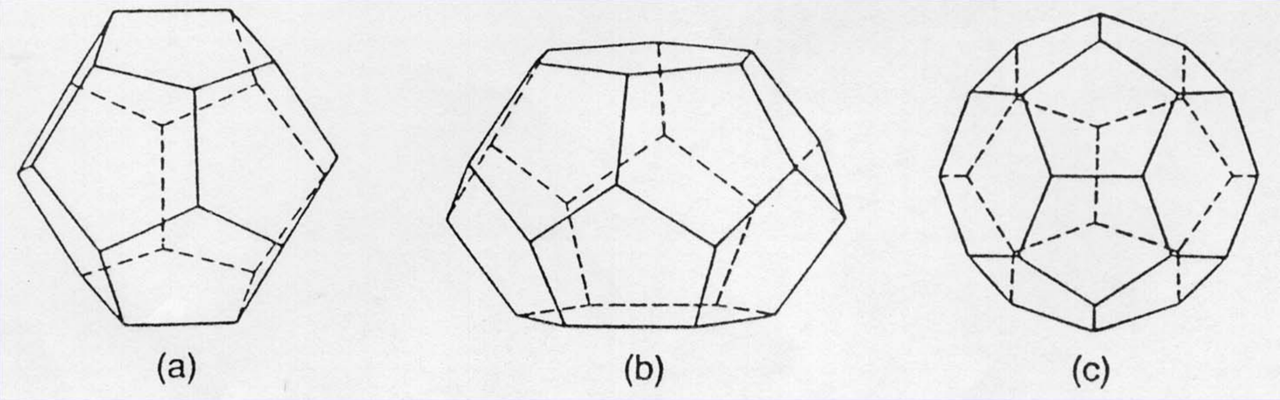
- Environmental problem
  - Releasing of methane hydrates at the bottom of the ocean and in permafrost regions might increase global warming.

A flame held over room-temperature hydrates will ignite the evaporating methane and result in "burning ice." New production techniques are now being developed in hopes that hydrates may become a major energy source in the future. (Source: GSJ Symposium on Methane Gas Hydrate on June 10, 1996.)

ate.org

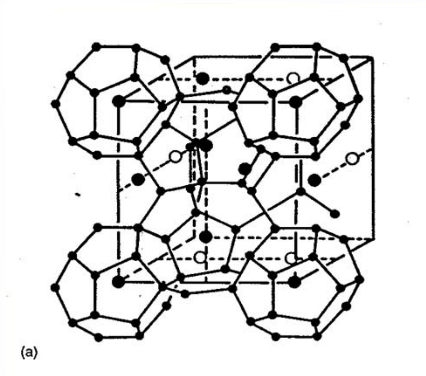
What are gas hydrates ?

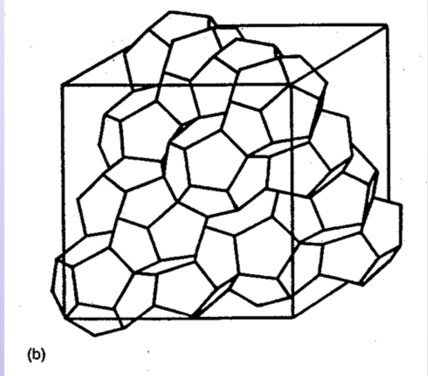
- Crystalline solids consisting of a guest(s) component(s) and water
- Hydrates can form at conditions above the normal freezing point of water by the hydorogen bonding.
- Three cavities in gas hydrates

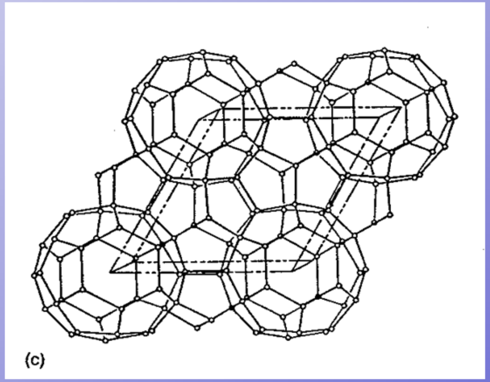


(a) Pentagonal Dodecahedron(5^{12}) (b)Tetrakaidecahedron($5^{12}6^{2}$) (c)Hexakaidecahedron($5^{12}6^{4}$)
(Reproduced from “*Clathrate Hydrates of Natural Gases*”, Sloan, 1998)

- Structures of gas hydrates







- Structure I(a) and II(b) form with relatively small guests, e.q., methane, ethane, nitrogene, etc.
- Structure I and II contains 48 and 136 water molecules, respectively.
- Structure H(c) is only known to form with at least one small guest (i.e., methane) and one large guest, e.q., cyclooctane, methylcylcohexane, etc.

Van der Waals and Platteeuw(vdWP) model

- The statistical thermodynamic model for determining hydrate equilibrium pressures and temperatures

$$\Delta\mu_w^H = \mu_w^{EH} - \mu_w^H = -RT\sum_j \nu_j \ln(1-\sum_i \Theta_{ji})$$

$$\Theta_{ji} = \frac{C_{ji}(T)\,f_i(T,P)}{1+\sum_k C_{jk}(T)\,f_k(T,P)}$$

- μ_w^{EH} is the chemical potential of the hypothetical empty hydrate.
- Langmuir constant, $C_{ji}(T)$ is calculated using Kihara potential, etc.
- $f_i(T,P)$ is the fugacity of guest component i and calculated by a equation of state.

Three Models for hydrate Phase Equilibria

- The chemical potential difference between the hypothetical empty hydrate and the fluid phase or ice is calculated by classical thermodynamic relations.
  - Holder et al.(*I&EC Fund.*,1980, 19, 282-286)
- A fugacity(or chemical potential) model for the empty hydrate
  - Klauda and Sandler(*I&EC*,2000, 39, 3377-3386)
    - Fitting the vapor pressure of the empty hydrate as guest components
    - Not applicable to the mixed hydrates
  - Yang et al.(*Fluid Phase Equilibria*, 2000, 175, 75-89, etc.)
    - Using the same value of vapor pressure of the empty hydrate irrespective of the kind of guest components
    - Applicable to the mixed hydrates and various phase equilibria

Holder et al.(1980)

- The chemical potential difference between the hypothetical empty hydrate and the fluid phase or ice

$$\frac{\mu_W^{EH}-\mu_W^{\Pi}}{RT}=\frac{\Delta\mu_W^{EH}(T_o,P_o)}{RT}-\int_{T_o}^{T}\frac{\Delta H_W^{EH}}{RT^2}dT+\int_{P_o}^{P}\frac{\Delta V_W^{EH}}{RT}dP-\ln x_w\gamma_w$$

$$\Delta H_W^{EH}=\Delta H_W^o+\int_{T_o}^{T}\left(\Delta C_P^o+a(T-T_o)\right)dT$$

- The parameters($\Delta\mu_W^{EH}, \Delta H_W^{EH}, \Delta V_W^{EH}$) are fitted with 3-phase equilibrim curve.
- The solubility of water are calculated with Henry’s law constant expression of Krichevsky and Kasarnovsky.

Klauda and Sandler(2000)-I

- The equality of fugacity for a hydrate in equilibrium with fluid phase is

$$f_W^H(T,P) = f_W^\Pi(T,P)$$

- The fugacity of water in the hydrate phase is

$$f_W^H(T,P) = \exp\left(\frac{\mu_W^H - \mu_W^o}{RT}\right) = \exp\left(\frac{\mu_W^H - \mu_W^{EH} + \mu_W^{EH} - \mu_W^o}{RT}\right)$$

$$= f_W^{EH}(T,P)\exp\left(\frac{-\Delta\mu_W^H(T,P)}{RT}\right)$$

- $f_W^{EH}(T,P)$ is the fugacity of the hypothetical empty hydrate.

$$f_W^{EH}(T,P) = P_W^{satEH}(T)\phi_W^{satEH}(T)\exp\left(V_W^{satEH}(T,P)(P - P_W^{satEH}(T))/RT\right)$$

Klauda and Sandler(II)

- The fugacities of ice and liquid water are

$$f_W^{ice}(T,P) = P_W^{ice}(T)\phi_W^{ice}(T)\exp\left(V_W^{ice}(T,P)(P-P_W^{ice}(T))/RT\right)$$

$$f_W^{L}(T,P) = x_W\gamma_W P_W^{sat,L}(T)\phi_W^{sat,L}(T)\exp\left(V_W^{sat,L}(T,P)(P-P_W^{sat,L}(T))/RT\right)$$

- The solubilities of guest components are calculated from

$$1-x_w = x_i = f_i^V / H_i \exp(Z_i^\infty)$$

- The PRSV equation of state is used because of its relative success with water

Klauda and Sandler(III)

- This model uses the publised Kihara cell potential parameters from viscosity and second virial coefficient data.

- Making the vapor pressure of empty hydrate dependent on the guest components improve the predictability to hydrate phase equilibria.

- Because the vapor pressure of the empty hydrate is guest dependent, a mixing rule for the vapor pressure parameters will be needed to extend the predictions to the mixed hydrates.

Yang et al.(2000)

- The equality of chemical potential for a hydrate in equilibrium with fluid phase(Π) is

$$\mu_W^{\Pi} - \mu_W^{0} = \mu_W^{H} - \mu_W^{0} = \mu_W^{H} - \mu_W^{EH} + \mu_W^{EH} - \mu_W^{o}$$

$$= -\Delta\mu_W^{EH} - RT\ln\left(P_W^{satEH}\phi_W^{satEH}\right) - V_W^{satEH}(P - P_W^{satEH})$$

- Assuming that the structure of the hypothetical empty hydrate is independent of guest molecules.
    - The vapor pressure of the empty hydrate is independent of guest molecules.
    - The Kihara cell potential parameters of each guest molecules are optimized with 3-phase equilibrium data.
    - Extended to mixed hydrates with ease.

Comparison of three models for methane hydrate

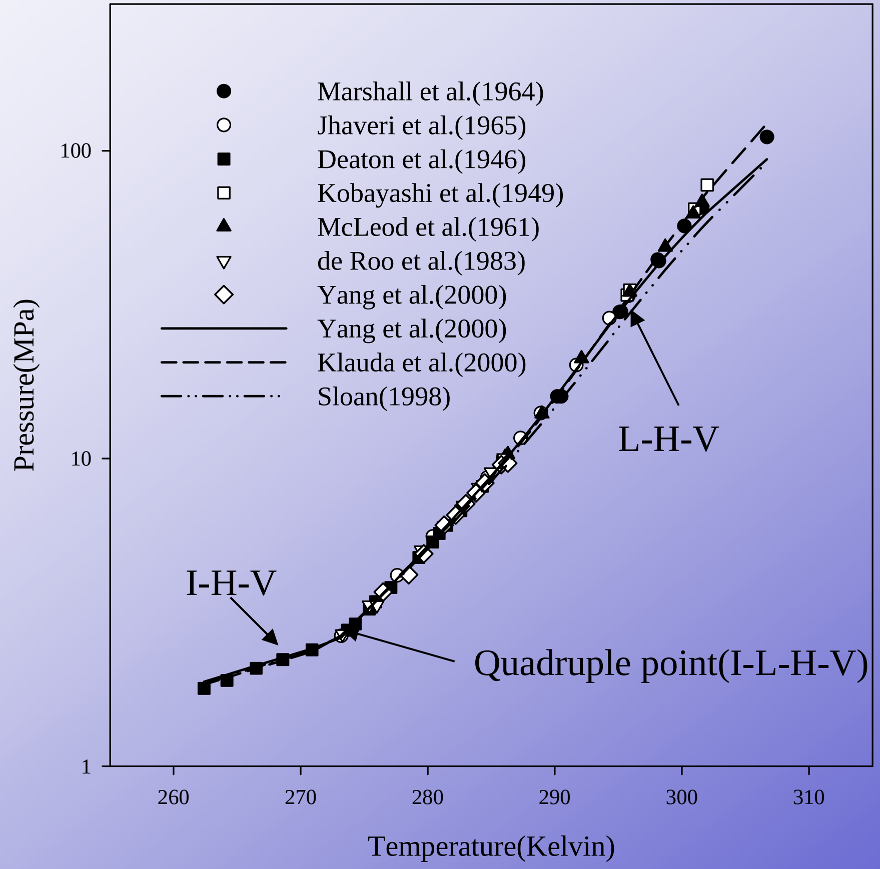


Figure 1. Comparison of experimental and calculated equilibrium pressure of methane hydrate in three-phase equilibria.

Comparison of three models for ethane hydrate

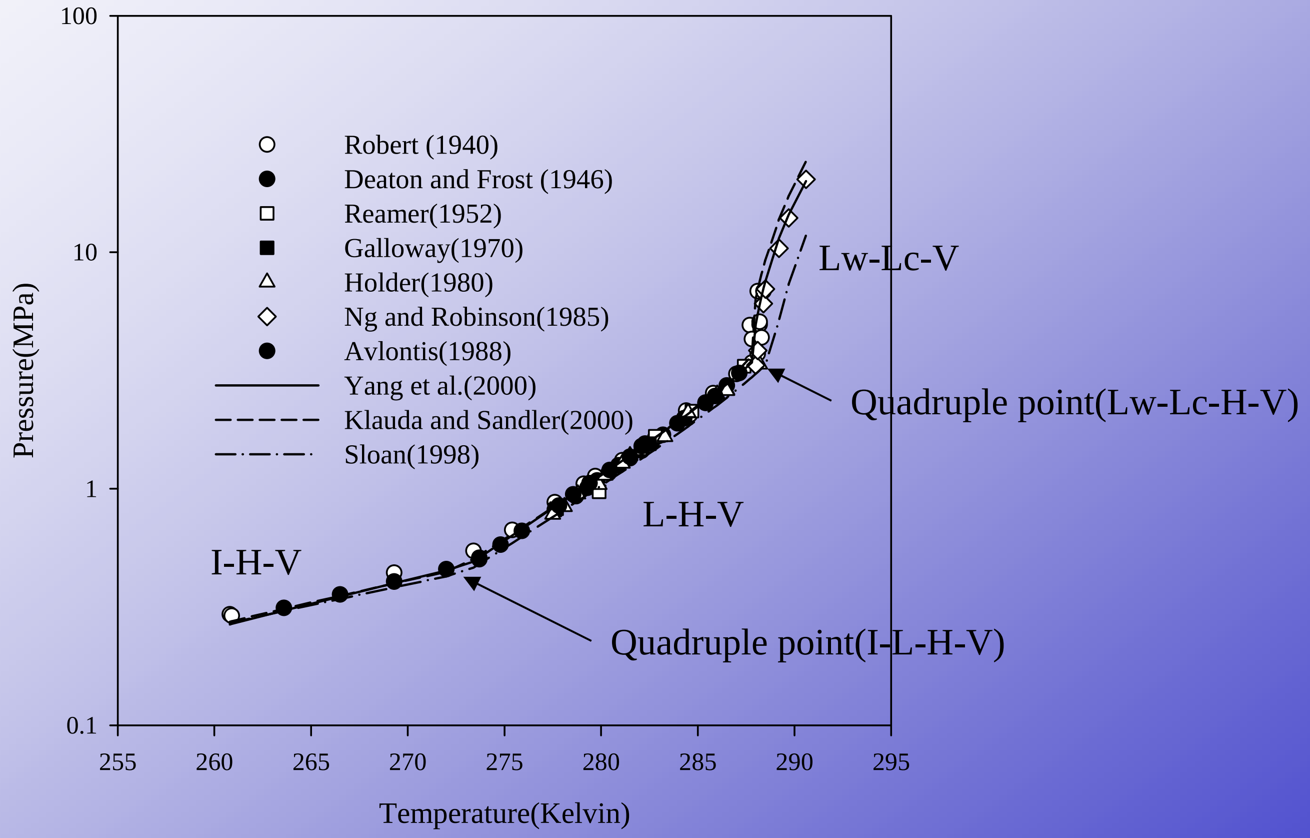


Figure 2. Comparison of experimental and calculated equilibrium pressure of ethane hydrate in three-phase equilibria.

Comparison of three models for carbon dioxide hydrate

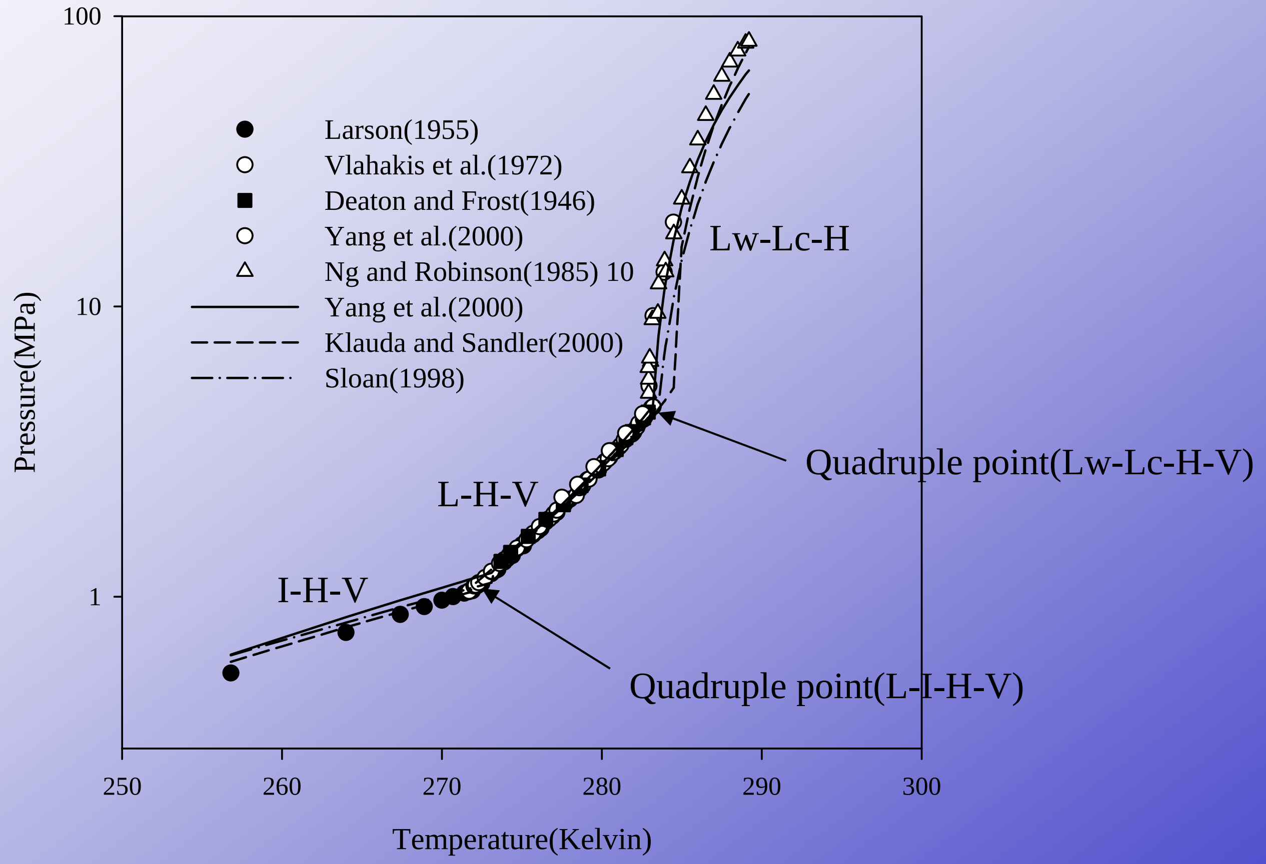


Figure 3. Comparison of experimental and calculated equilibrium pressure of carbon dioxide hydrate in three-phase equilibria.

Comparison of Three Models

- % AAD from Experiments

	Methane			Ethane				Carbon dioxide			
Phase	IHV	LHV	overall	IHV	LHV	LLH	overall	IHV	LHV	LLH	overall
Sloan	1.62	7.19	6.79	6.74	8.78	35.79	13.70	5.69	2.69	40.55	9.82
Klauda and Sandler	1.42	2.77	2.68	4.04	5.24	41.6	11.99	2.32	3.25	37.62	9.52
Yang et al.	2.79	3.26	3.23	5.15	3.47	18.49	6.44	11.68	1.99	22.05	6.25

$$\%AAD = \frac{1}{N}\sum_{i}^{N}\left|\frac{P_{i,\exp} - P_{i,cal}}{P_{i,cal}}\right| \times 100$$

Conclusion

- The fugactiy or chemical potential model (Klauda et al. or Yang et al.) is more accurate than the classical thermodynamic model(Holder et al.) for the prediction of hydrate equilibrium pressures.
- A mixing rule for the vapor pressure parameters will be needed to extend the predictions to the mixed hydrates for Klauda’s model.
- Yang’s model is applicable to the mixed hydrates and various phase equilibria relatively with ease.