Measurements and Predictions of Phase Equilibria for Water + Ethane in Hydrate-Forming Conditions

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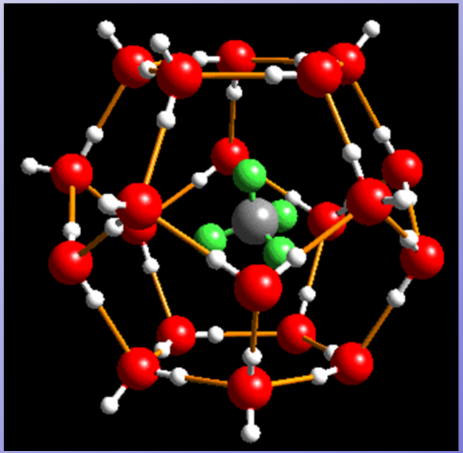
Introduction

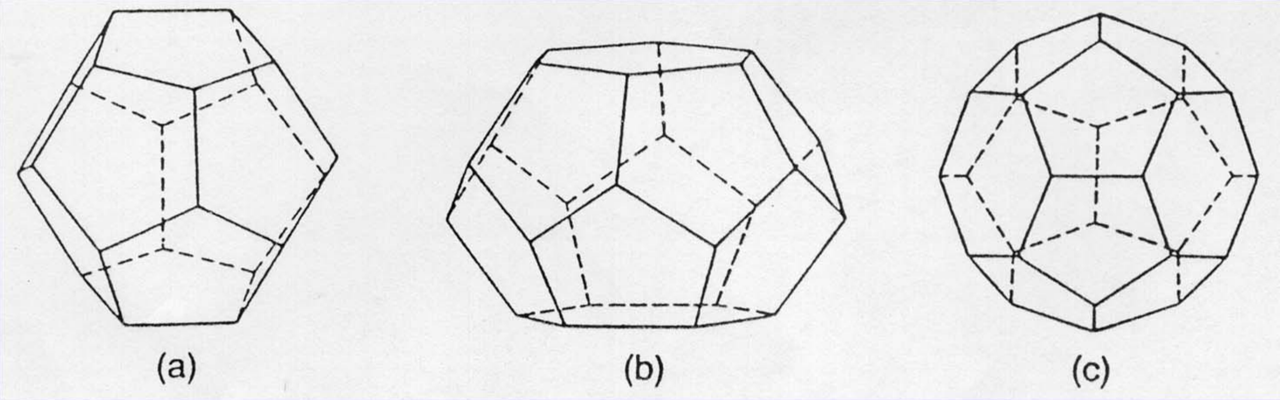
- Gas Hydrate (Clathrate Hydrate)
  - a solid solution of water and light gases through hydrogen bonding



- Researches on the gas hydrate
  - Methane hydrates as a future resource of energy
  - Carbon dioxide sequestration as hydrates in deep ocean
  - Process problems in petroleum industry
    - Effects of inhibitors on hydrate-forming condition
    - Prediction of phase equilibria for mixed hydrates

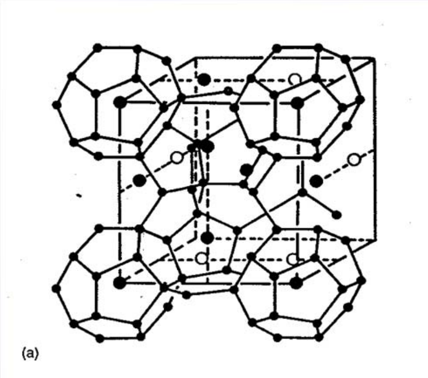
What are gas hydrates ?

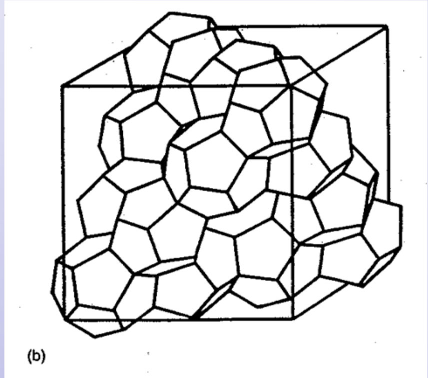
- Crystalline solids consisting of a guest(s) component(s) and water
- Hydrates can form at conditions above the normal freezing point of water by the hydorogen bonding.
- Three cavities in gas hydrates

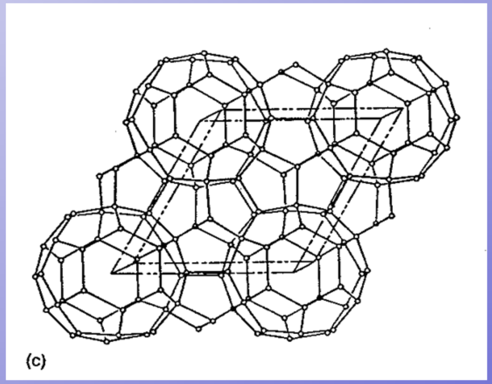


(a) Pentagonal Dodecahedron(5^{12}) (b)Tetrakaidecahedron($5^{12}6^{2}$) (c)Hexakaidecahedron($5^{12}6^{4}$)
(Reproduced from "*Clathrate Hydrates of Natural Gases*", Sloan, 1998)

- 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.

Studies on Ethane Hydrate

- $H\text{-}L_W\text{-}V_{C2H4}$ and $H\text{-}I\text{-}V_{C2H4}$
  - Roberts et al.(1940) …
- $H\text{-}L_W\text{-}L_{C2H4}$
  - Ng and Robinson(1985)
- $H\text{-}\Pi_{C2H4}$
  - Sloan(1986)
  - Song and Kobayashi(1994)

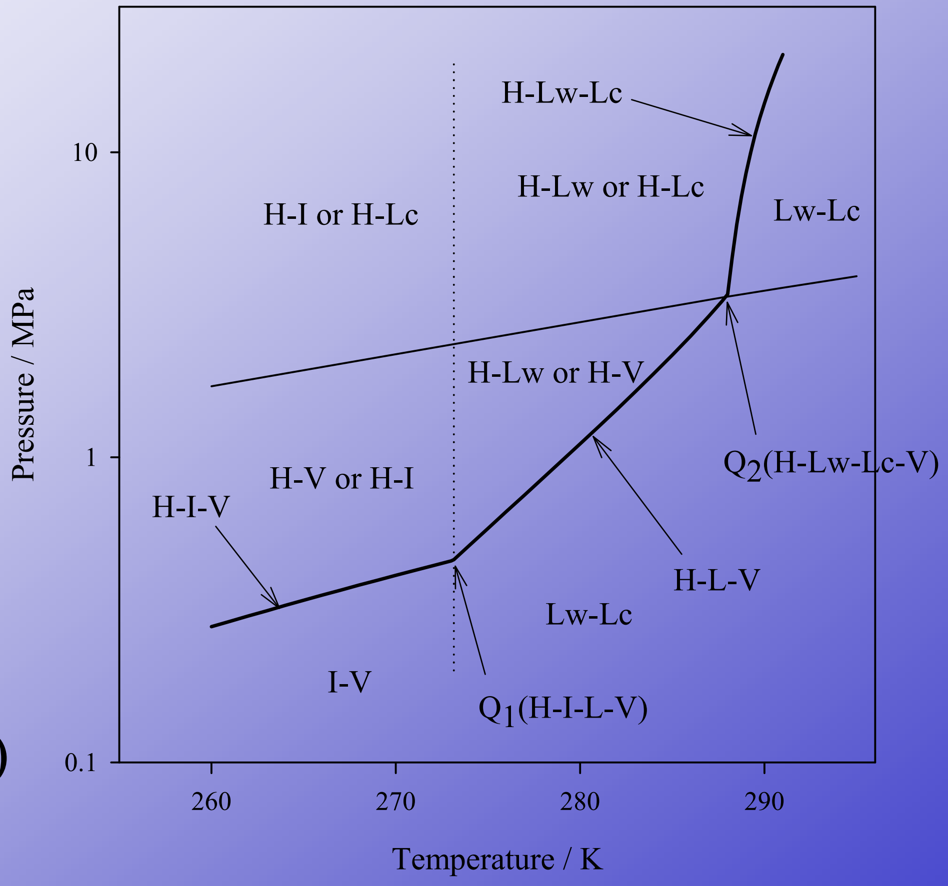


Figure 1. Phase diagram of H_2O - C_2H_6

Models on Gas Hydrate

- Van der Waals and Platteeuw [1959]
  - Statistical model of hydrate cavities similar to gas adsorption model by Langmuir
- Holder et al.[1980]
  - The chemical potential difference between the hypothetical empty hydrate and the fluid phase or ice is calculated by classical thermodynamic relations
- Klauda and Sandler(2000)
  - Fitting the vapor pressure of the empty hydrate for each guest component

Purpose

- Experimental determination of H-L_W equilibria
  - Effect on ethane solubility by existence of NaCl

- EOS approach available on
  - three-phase equilibria (**H-I-V_{C2H6}, H-L_W-V_{C2H6} , H-L_W-L_{C2H6}**)
  - two-phase equilibria (**H-L_W , H-L/V_{C2H6}**)

- Applicability of Nonramdom Lattice Fluid Thoery (NLF-HB) and Gibbs energy model on hydrate containing equilibria

NLF-HB Equation of State

- Nonrandom Lattice Fluid Hydrogen Bonding Theory
  - NLF EOS by You et al. [1993 a, b]
  - Expansion to associating system using Veytsman statistics[1990] by Yeom et al. [1999]
  - A normalization of Veytsman statistics by Lee et al. [2000]
- Parameters for pure species

$$\varepsilon_{ii} / k = \varepsilon_a + \varepsilon_b (T - 273.15) + \varepsilon_c [T \ln(273.15 / T) + (T - 273.15)]$$

$$r_i = r_a + r_b (T - 273.15) + r_c [T \ln(273.15 / T) + (T - 273.15)]$$

- Hydrogen-bonding energy and entropy for H_2O-H_2O interaction
  - $E_{HB}^0 = -15.5\ kJ/mol$, $S_{HB}^0 = -16.5\ J/mol\text{-}K$ by Luck [1980]

NLF-HB Equation of State

- Expression for Pressure

$$P=\frac{1}{\beta V_H}\left\{\left(\frac{z}{2}\right)ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-ln(1-\rho)-\nu_{HB}\rho\right\}-\left(\frac{z}{2}\right)\theta^2\left(\frac{\varepsilon_M}{V_H}\right)$$

$$\varepsilon_M=(1/\theta^2)\sum\sum\theta_i\theta_j\varepsilon_{ij}+(\beta/2\theta^2)\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})$$

$$\rho_i=N_ir_i/(N_0+\sum_{i=1}^{C}N_ir_i) \qquad \theta_i=N_iq_i/(N_0+\sum_{i=1}^{C}N_iq_i)$$

$$\nu_{HB}=\left(\sum_{k=1}^{K}\sum_{l=1}^{L}N_{kl}^{HB}-\sum_{k=1}^{K}\sum_{l=1}^{L}N_{kl}^{HB0}\right)/\sum_{i=1}^{C}N_ir_i$$

- Expression for chemical potential

$$\frac{\mu_i^{\Pi}-\mu_i^{\Pi 0}}{RT}=-ln\left(\frac{V_H}{RT}\right)+r_i\,ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-r_i\,ln(1-\rho)+ln\left(\frac{\theta_i}{q_i}\right)+\left(\frac{z\beta q_i\varepsilon_M\theta^2}{2}\right)$$

$$\times\left[1-\frac{r_i}{q_i}-\frac{2\sum\theta_k\varepsilon_{ik}+\beta\sum\sum\sum\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+2\varepsilon_{kl}-2\varepsilon_{jk}-\varepsilon_{ik})}{\varepsilon_M\theta^2}\right]+\sum_{k=1}^{m}d_k^i\,ln\frac{N_{k0}^{HB}}{N_{k0}^{HB0}}+\sum_{k=1}^{n}a_k^i\,ln\frac{N_{0k}^{HB}}{N_{0k}^{HB0}}$$

Thermodynamic Model for Hydrate Phase Equilibria

- Hydrate phase by van der Waals and Platteeuw model(1959)

$$\mu_W^H = \mu_W^{EH} + RT\sum_j \nu_j \, ln[1 - C_{i,j} f_i^{\Pi} /(1 + C_{i,j} f_i^{\Pi})]$$

$$f_i^{\Pi} = P^0 \, exp[(\mu_i^{\Pi} - \mu_i^{\Pi 0})/RT]$$

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

- Chemical potential difference between empty hydrate and reference fluid state

$$\mu_W^{EH} = \mu_W^{\Pi 0}(T_0, P_0) + \int_{T_0}^{T} (\Delta H_W^{H\Pi} / RT^2)dT + \int_{P_0}^{P} (\Delta V_W^{H\Pi} / RT)dP$$

$$\mu_W^{EH} = \mu_W^{\Pi 0} + RT \, ln[\, f_{pureW}^{EH} / f_{pureW}^{\Pi}\,]$$

$$= \mu_W^{\Pi 0} + RT \, ln[\, P_W^{EH} \phi_W^{EH} / P \varphi_{pureW}^{\Pi}\,] + \Delta V_W^{EH}[\, P - P_W^{EH}\,]$$

$$\ln[P_W^{satEH} / atm] = 17.410 - 6072.3/[T/K]$$

Chemical Equility

- Three-phase equilibria

$$\mu_i^{\Pi(1)} = \mu_i^{\Pi(2)}$$

$$\mu_W^{\Pi} - \mu_W^{\Pi 0} = \mu_W^{H} - \mu_W^{\Pi 0}$$

$$\mu_W^{H} - \mu_W^{\Pi 0} = RT \sum_j \nu_j \, ln[1 - C_{i,j} f_i^{\Pi} /(1 + C_{i,j} f_i^{\Pi})]$$

$$+ RT \ln[P_W^{EH} \phi_W^{EH} / P \varphi_{pureW}^{\Pi}] + \Delta V_W^{EH} [P - P_W^{EH}]$$

- Two-phase equilibria

$$\mu_W^{\Pi} - \mu_W^{\Pi 0} = \mu_W^{H} - \mu_W^{\Pi 0}$$

- Phase equilibria for containing electrolyte

$$\mu_i^{L} = \mu_{i,EoS}^{L} + RT \ln a_i^{E}$$

Pure parameters for NLF-HB EOS

- Pure parameter regression
  - Vapor pressure and saturated liquid & vapor density

Table 1. Pure parameters for NLF-HB EOS

	ε_a	ε_b	ε_c	r_a	$r_b\times10^3$	$r\times10^3{}_c$
H_2O	134.022	7.8×10^{-5}	-0.229	1.727	-0.002	-3.749
C_2H_6	76.378	-4.9×10^{-7}	-0.110	5.091	-0.007	10.384

$$\varepsilon_{ii}/k=\varepsilon_a+\varepsilon_b(T-273.15)+\varepsilon_c[T\ln(273.15/T)+(T-273.15)]$$

$$r_i\;=r_a+r_b(T-273.15)+r_c[T\ln(273.15/T)+(T-273.15)]$$

- Hydrogen-bonding parameters for H_2O-H_2O interaction

$$E_{HB}^0=-17.95\;\;kJ/mol\qquad S_{HB}^0=-16.6\;\;kJ/mol$$

Gibbs Energy Model(Lee et al., 1996)

- Pure parameter
  - Solvent or non-ionic molecule : 2 parameters
  - Ion : 3 parameters

Components	$r_{s,j}[\AA]$	$r_j[\AA]$	$\varepsilon_{ii}[kJ/mol]$
Water	-	2.500	2.062
Ethane	-	6.3056	0.1733
Na^+	2.327	2.554	5.521
Cl^+	3.017	0.484	1.362

- H_2O – C_2H_6 interaction parameter

  $k_{ij}=0.6276-187.123/T[K]$

Experimental Apparatus

- System accuracy
  - Pressure : ±0.06 MPa
  - Temp. : ±0.05 K
  - Mole fraction : 5.3%
  - Reproducibility of syringe pump : 0.5%

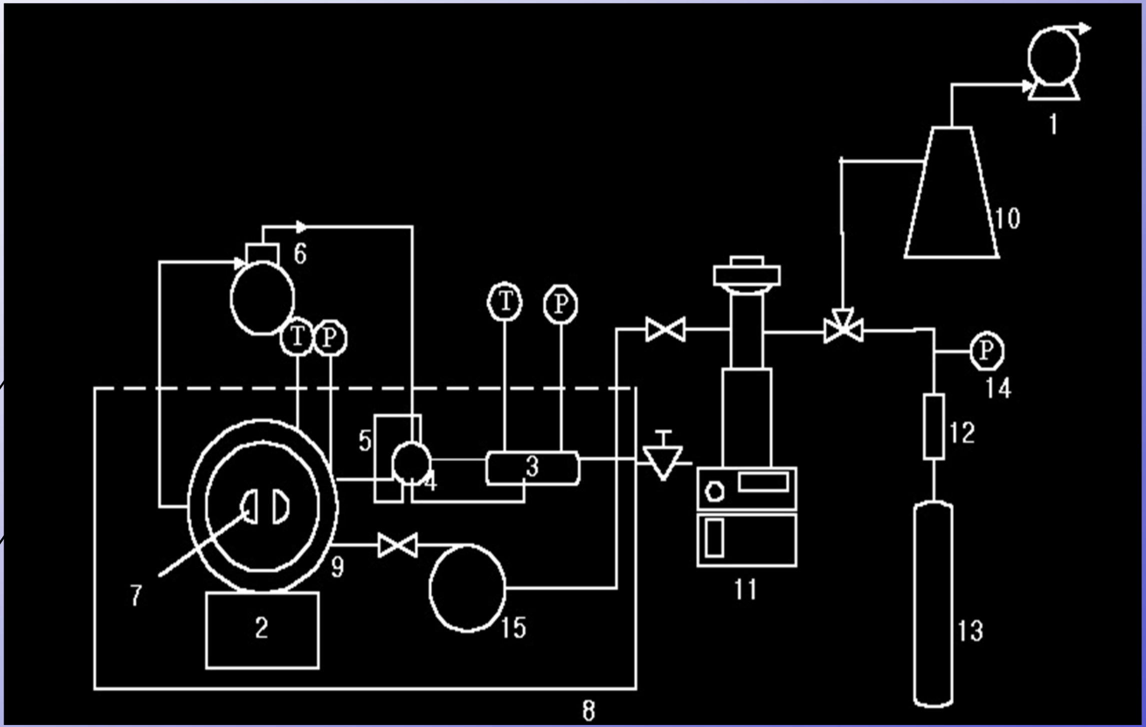


Figure 2. **The experimental apparatus for measurement of the equilibrium pressure and the solubility of dissolved gas in the hydrate containing equilibria**

(1)vacuum pump; (2)magnetic stirrer; (3)sampling cell; (4)sampling valve; (5)sampling loop; (6)metering pump; (7)density transducer; (8)water bath; (9)equilibrium cell; (10)flask; (11)syringe pump; (12)line filter; (13)gas bomb; (14) pressure gauge (15) McHugh type variable volume view cell

V_{CH4}-L_W equilibria

- Binary parameter for C_2H_6-H_2O

  $k_{ij} = 0.90994 - 195.56/T$

Table 2. Calculated L_W-V_{C2H6} equilibrium composition

NaCl	pts	AADx [%]	P range [bar]	Type
0	8	4.3	13.7-35.4	a
0	4	11.0	24.4-36.1	b
1 M	3	26.7	32.2-57.4	a

a) Mole fraction of ethane in water rich phase

b) Mole fraction of watee in ethane rich phase

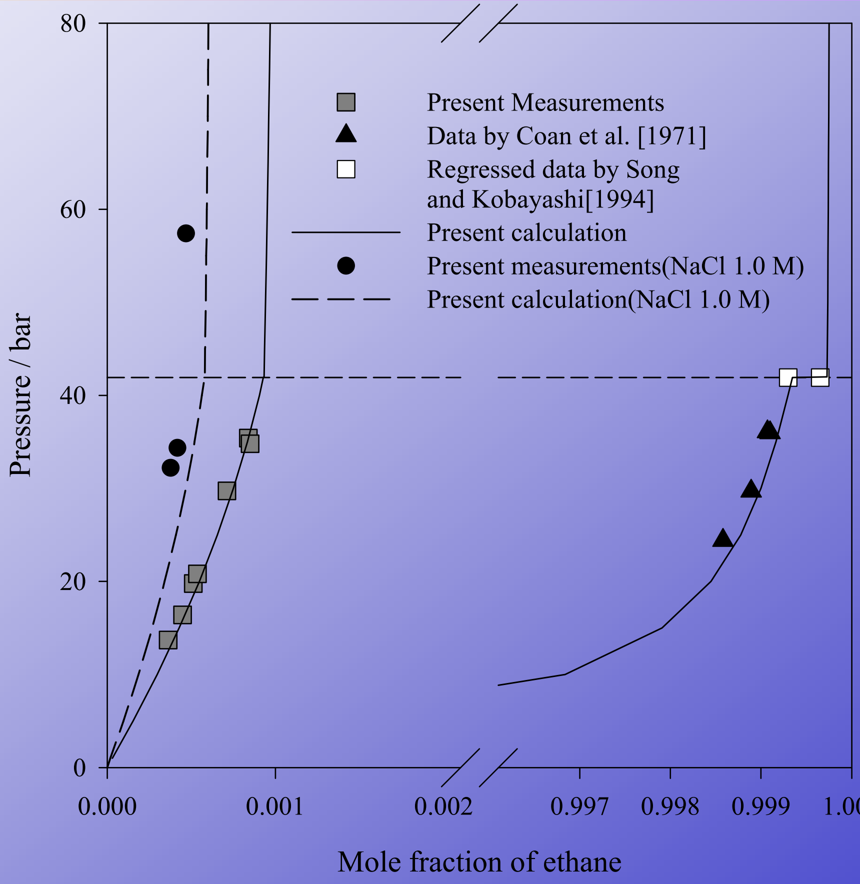


Figure 3. Isothermal vapor-liquid equilibria for water +ethane system at 298.15 K

Three-phase equilibria

Table 4. Kihara potential for ethane hydrate

	ε/*k* [K]	σ[Å]	$a^{a)}$ [Å]
C_2H_6	144.7597	3.2606	0.5651

a) Radius of the spherical core(*a*) was from Sloan(1998)

Table 5. Comparison of calculated 3-phase equilibrium pressure

Phase	pts	Calculated error a)		
		Present	Sloan	Klauda
$H\text{-}I\text{-}V_{C2H6}$	7	2.8	6.8	4.0
$H\text{-}L_W\text{-}V_{C2H6}$	61	2.6	9.0	5.2
$H\text{-}L_W\text{-}L_{C2H6}$	17	15.4	35.8	-

a) Absolute Average Deviation in pressure

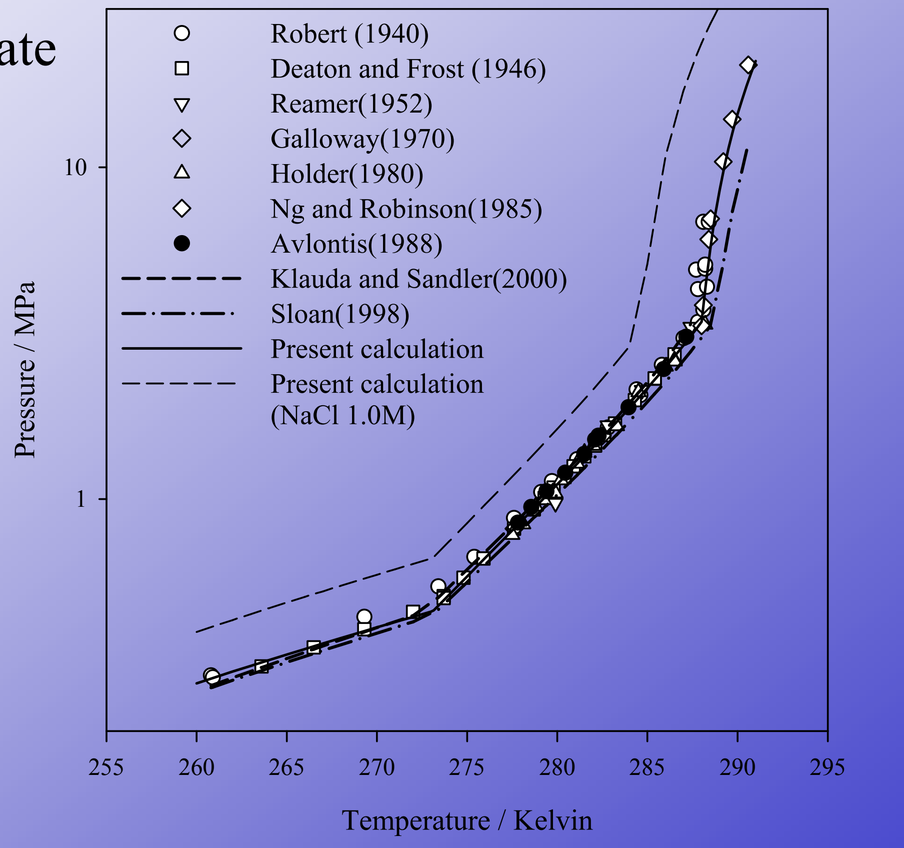


Figure 4. Comparison of experimental and calculated equilibrium pressure of ethane hydrate in three-phase equilibria.

H-Π_{C2H6} Equilibria

Table 6. Comparison of calculated Water content in ethane rich phase

Phase	pts	Sloan[a)] [%]	Present[a)] [%]
H-V_{C2H6}[b)]	3	69.3	21.6
H-L_{C2H6}[b)]	4	14.0	16.1
H-L_{C2H6}[c)]	6	16.6	29.2

a) absolute Average Deviation in mole fraction

b) Song and Kobayashi(1994)

c) Sloan et al.(1986)

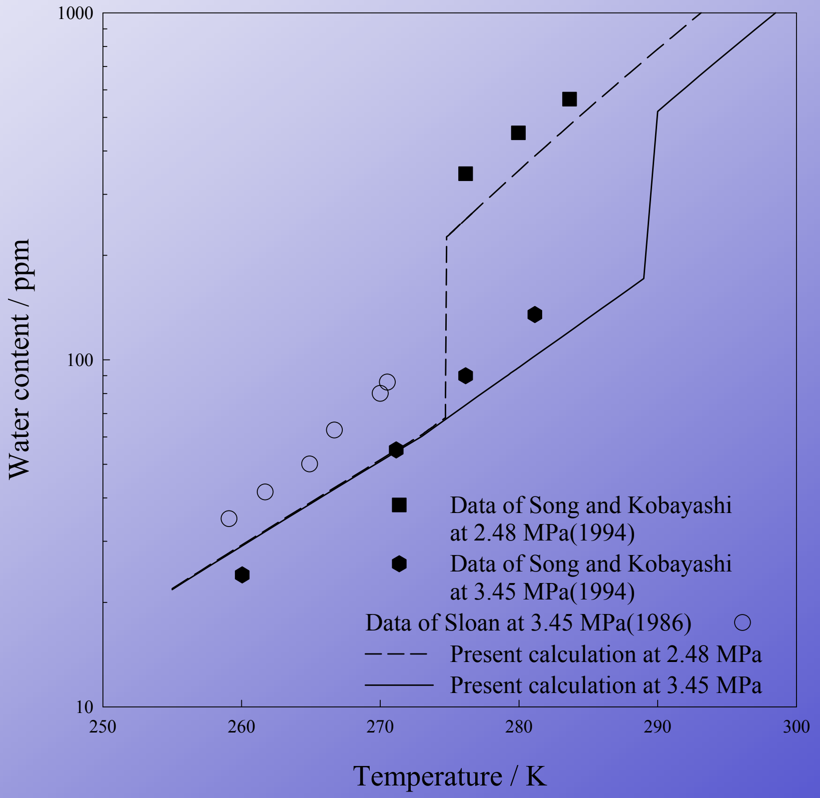


Figure 5. Comparison of calculated water contents in ethane-rich phase of H-L/V_{C2H6} equilibria with data of Sloan et al. (1986) and Song and Kobayashi (1994)

H-Lw equilibria

Table 7. Comparison of calculated Ethane solubility in water phase

NaCl	pts	AADa)[K]
0	3	0.09
1 M	3	4.84

a) Absolute Average Deviation in temperature(K)

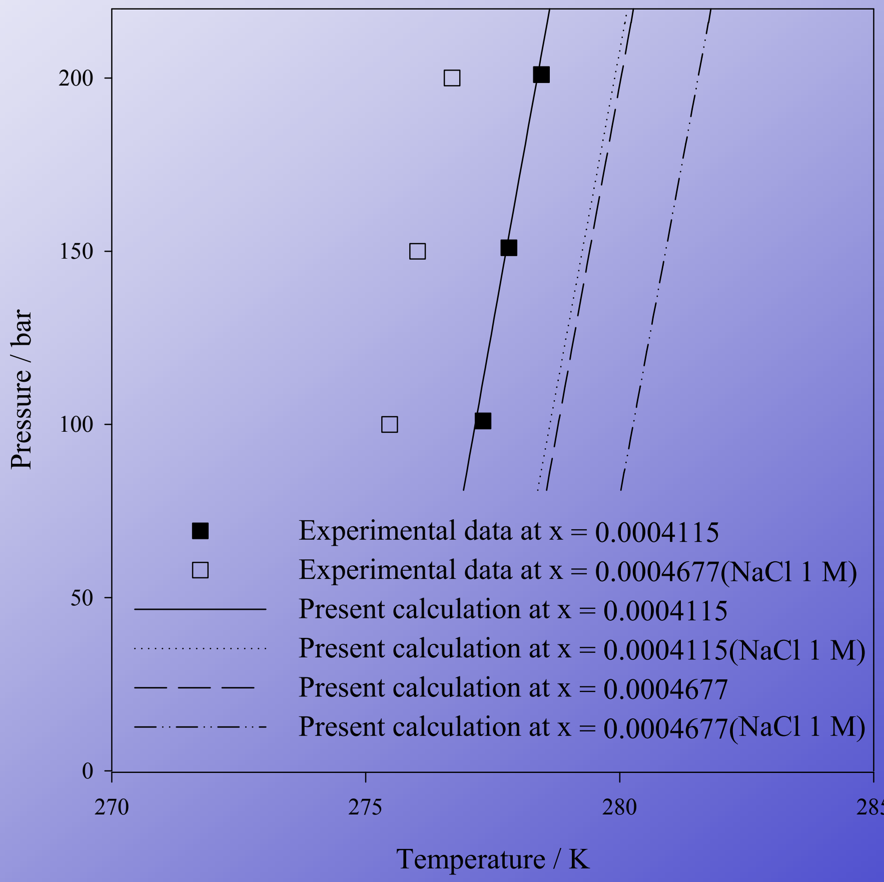


Figure 6. Comparison of present calcualtion and experimental data of H-Lw equilibria of ethane hydrate

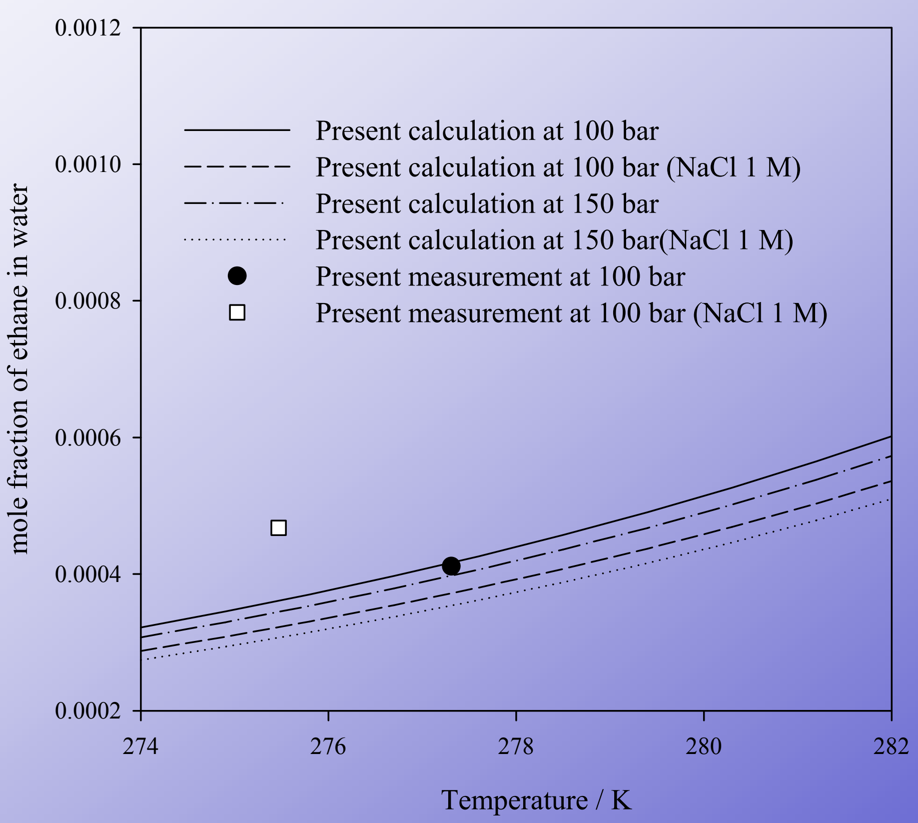


Figure 7. Comparison of calculated isobaric solubility of ethane in liquid water phase of H-Lw equilibria with experiments at 100 bar

Conclusion

- H-Lw Equilibrium compositions of ethane were experimentally determined.

- Recently proposed NLF-HB EOS was applied to various hydrate-containing phase equilibria.

- Effects of salt on hydrate-containing phase equilibria were experimentally determined for H-Lw equilibria and predicted for three-phase ($H\text{-}I\text{-}V_{C2H6}$, $H\text{-}L_W\text{-}V_{C2H6}$, $H\text{-}L_W\text{-}L_{C2H6}$) and two-phase ($H\text{-}L_W$) equilibria.