Gas Hydrates in the Presence of Aqueous Electrolyte, Alcohol and Glycol Solutions: Experiments and Modelling

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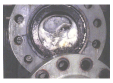
Practical Background



- Hydrate formation and deposition in gas transmission lines under high pressure and ambient temperature causing operational hazards and production losses.

⇒ Prevention of hydrate formation by injection of inhibiting agents like methanol or glycols.

- Natural gas hydrate occurence in permafrost regions and in marine sediments.

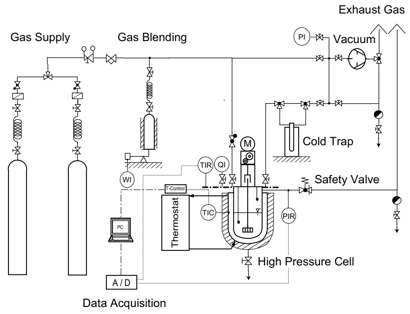
⇒ Potential future energy resource.

Accurate predictive methods for hydrate equilibrium calculations required to design economically and safely operating hydrate inhibition utilities in natural gas production, and to evaluate natural gas hydrate location and stability.

Project Aims

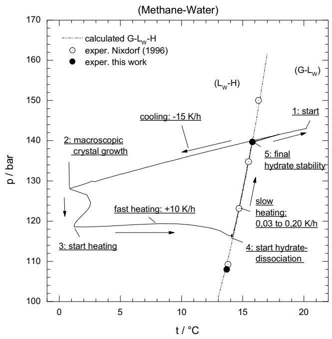
- Further development and extension of calculational method to predict hydrate equilibria in multi-phase aqueous systems containing mixed electrolytes and organic inhibitors.
- Thermodynamically consistent prediction of macroscopic hydrate equilibrium and microscopic and structural properties for mixed gas hydrates over an extended range of temperature and gas composition.
- Generation of reliable and systematically consistent own data base needed for model development.
- Optimization of appropriate experimental method to avoid systematical errors entailed by kinetic effects of hydrate decomposition.

Experimental I: Apparatus



Essential features:
- Tempered double shell high pressure cell (stainless steel; 1000 ml; 300 bar).
- High performance magnetic stirrer.
- Computer aided data acquisition and temperature control.

Experimental II: Isochoric Method



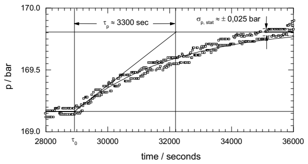
Procedure: pressure-temperature "loop"

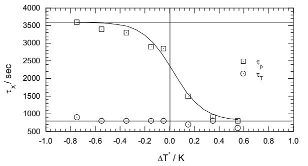
1. Start: system equilibration in the 2-phase region (G-LW).
2. Hydrate formation: macroscopic crystal growth from subcooled (metastable) states.
3. Reheating: quick approach to thermodynamic hydrate stability border.
4. Hydrate dissociation: slow (quasi-static) heating.
5. Final hydrate stability (equilibrium) condition: dissociation of the "last" hydrate crystal detected from unsteady change of slope of the heating trace.

Experimental III: Kinetics of Dissociation

Time resolved measurement: transient response of system pressure (X = p) and temperature (X = T) to an incremental increase of shell temperature. Macroscopic first order kinetic approach:

$$X(\tau) = X_0 + \Delta X_{\max}\left(1 - \exp\left\{-\frac{\tau - \tau_0}{\tau_X}\right\}\right)$$





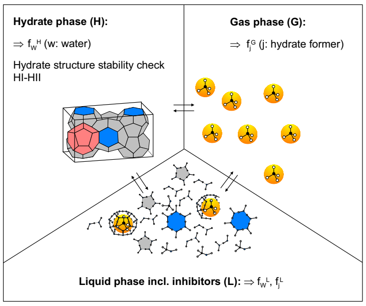
ΔT^* : Distance to equilibrium temperature.

Optimized experimental procedure:
Adjustment of mean heating rates to individually observed transient behavior.

Modelling of 3-Phase-Equilibrium (G-L$_W$-H)

Numerical solution of the "iso-fugacity criterion":

$$f_j^G = f_j^L = f_j^H$$
$$f_W^L = f_W^H$$



Hydrate phase (H):

⇒ f_W^H (w: water)

Hydrate structure stability check HI-HII

Gas phase (G):

⇒ f_j^G (j: hydrate former)

Liquid phase incl. inhibitors (L): ⇒ f_W^L, f_j^L

Solid Hydrate Phases:

Statistical Theory of van der Waals and Platteeuw (1959)

$$f_W^H = f_{oW}^L \exp\left\{\frac{\Delta\mu_{oW}^{\beta-L} - \Delta\mu_W^{\beta-H}}{RT}\right\}$$

$$\Delta\mu_W^{\beta-H} = RT\sum_i \nu_i \ln\left(1 + \sum_j C_{ij}(T) f_j^G\right)$$

$$C_{ij}(T) = \frac{4\pi}{kT}\int_{r=0}^{R^f} \exp\left\{-\frac{\varpi_{ij}(\sigma_{ij},\varepsilon_{ij},a_j,r)}{kT}\right\} r^2\,dr$$

$$\frac{\Delta\mu_{oW}^{\beta-L}(T,p)}{RT} = \frac{\Delta\mu_{oW,0}^{\beta-L}}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_{oW}^{\beta-L}(T)}{RT^2}dT + \int_{p_0}^{p}\frac{\Delta v_{oW}^{\beta-L}(p)}{RT}dp$$

C_{ij}: Langmuir coefficient of hydrate former (guest) j in hydrate cavity of type i
f_W^H: fugacity of water in the hydrate phase
f_{oW}^L: fugacity of pure liquid water
f_j^G: fugacity of hydrate former j in the gas phase
R^f: free cavity Radius
ϖ_{ij}: Kihara potential energy of hydrate former j in hydrate cavity i
$\Delta\mu_{oW}^{\beta-L}$: reference chemical potential difference between empty hydrate water lattice and pure liquid water

Here: calculation of smooth Kihara-cavity potential ϖ_{ij} with effective molecular parameters

$$\sigma_{ij} = \frac{\sigma_j^o + \sigma_W}{2}(1 - k_{ij}^\sigma);\ \varepsilon_{ij} = \sqrt{\varepsilon_j^o \varepsilon_W}\,(1 - k_{ij}^\varepsilon);\ a_j = \frac{a_j^o}{2}$$

Guest-cavity interaction parameters (k_{ij}^σ, k_{ij}^ε) specific for each pair cavity type i - guest j adjusted to experimental hydrate equilibrium data.

Fluid Phases:

Cubic equation-of-state (SRK: Soave-Redlich-Kwong)

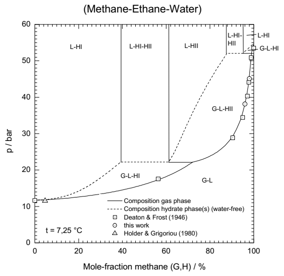
$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)}$$

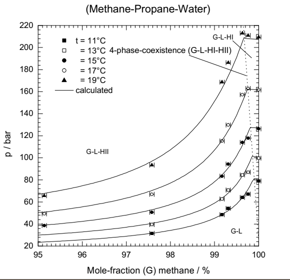
Aqueous Phase Mixing Effects:
Combination of Excess Gibbs Energy (G^E) model (Li et al., 1994) with SRK-EOS using the PSRK-mixing rule (Holderbaum, 1991)

$$\overline{G}^E = \overline{G}^{E(LR)} + \overline{G}^{E(MR)} + \overline{G}^{E(SR)}$$

Additive contributions from long range (LR) electrostatic interactions, middle range (MR) interactions between ionic species and solvents and short range (SR) interactions between (virtually) uncharged species.

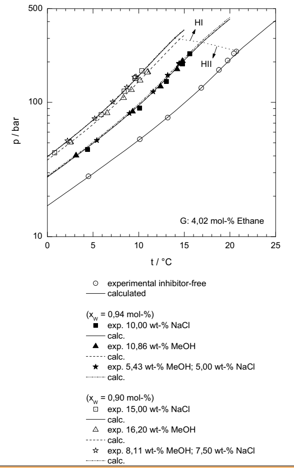
Results I: Incipient Hydrate Equilibrium Conditions and Structural Behavior for Inhibitor-free Mixtures





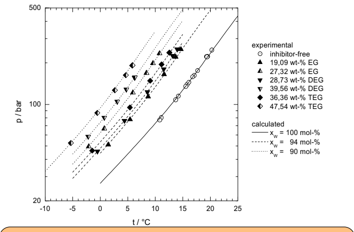
Temperature- and composition-dependent changes of stable hydrate structure in methan-ethane- and methane-propane-water systems.

Results II: Incipient Hydrate Equilibrium in the System Methane-Ethane-Water-Methanol-Sodium Chloride



Predominant influence of total inhibitor liquid mole-fractions (completely dissociated electrolytes) on hydrate formation temperature depression.

Results III: Glycol Inhibition of Methane-Hydrate Formation



For equal inhibitor liquid mole-fractions the hydrate formation temperature depression increases in the order EG < DEG < TEG

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