Thermodynamic modelling of systems containing water and hydrate inhibitors application to flow assurance and gas processing

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Outline

- Presentation of the research group
- Introduction
- Thermodynamic Modelling
- Results – Discussions
  - HSZ in The Presence of High Concentration of Inhibitor(S) or Salt(S)
  - HSZ of Oil/Condensate in the Presence of Produced Water and Inhibitors
  - Hydrate Inhibitor Distribution in Multiphase Systems
  - Gas Hydrate in Low Water Content Gases
- Remarks and Conclusions

- Background
  - *PVT and Phase Behaviour of Petroleum Reservoir Fluids research started in 1978*
  - *Gas hydrate research started in 1986*
  - *Centre for Gas Hydrate Research Established in Feb 2001*
  - *Centre for Flow Assurance Research (C-FAR) started in 2007*
- Areas of Activities
  - *Research*
  - *Consultancy*
  - *Training (open and in-house courses)*

Research Interests

- PVT and Phase Behaviour of Reservoir Fluids and CO_2-Rich Systems
- Flow Assurance
  - *Gas Hydrates*
  - *Wax*
  - *Salt (halite)*
  - *Asphaltene*
- Gas Hydrates
  - *Flow Assurance*
  - *Gas Hydrates in Sediments*
  - *Positive/other Applications of Gas Hydrates*

What are gas hydrates ?

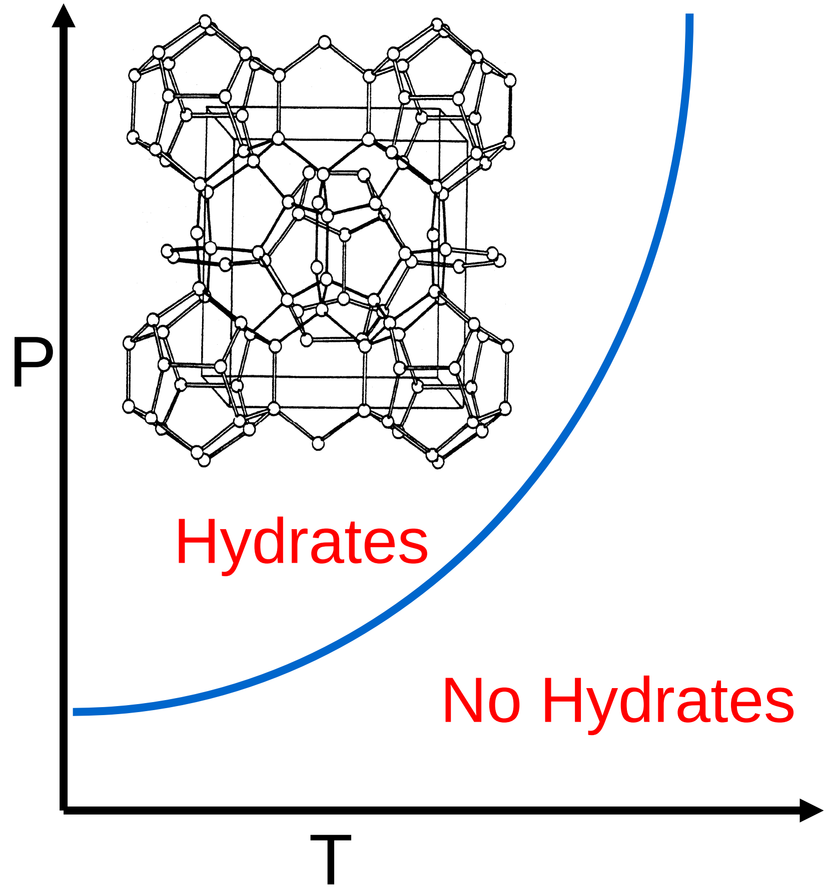
- Gas hydrates or *clathrate hydrates* are:
  - Ice-like crystalline compounds
  - Composed of water + gas (e.g. methane, CO_2)
  - Formed under low temperatures and elevated pressures
  - Stable well above the ice-point of water

Methane hydrate: the burning snowball

CENTRE FOR GAS HYDRATE RESEARCH

Hydrate Structures and Stability Zone

- The necessary conditions:
  - *Presence of water or ice*
  - *Suitably sized gas/liquid molecules (such as C_1, C_2, C_3, C_4, CO_2, N_2, H_2S, etc.)*
  - *Suitable temperature and pressure conditions*
- T and P conditions is a function of gas/liquid and water compositions.
- *Can form anywhere that the above conditions are met*



Hydrate phase boundary

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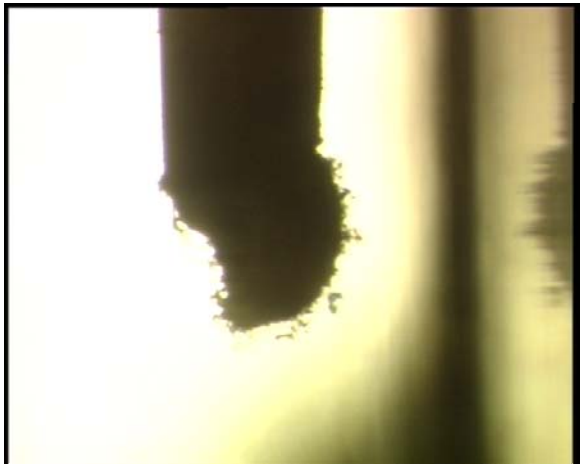
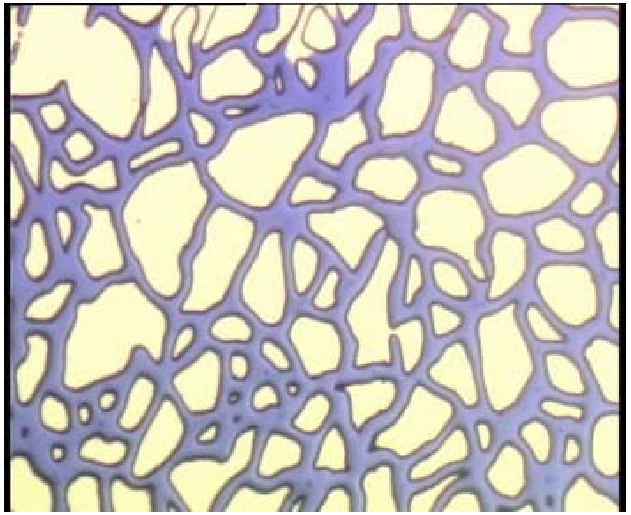
Gas Hydrate Formation

- *Not necessary:*
  - –Presence of a gas phase
  - –Presence of a free water phase
  - –Very low temperature conditions
  - –Very high pressure conditions





Gas Hydrate Formation

- *The extent of hydrate formation and the resulting problems depends on:*
  - The amount of water and hydrate forming compounds
  - Pressure and temperature conditions
  - Amount of thermodynamic or kinetic inhibitors
  - Presence of natural inhibitors
  - Other factors, such as, growth modifiers, local restriction, fluid type, pipe wall characteristics, etc.

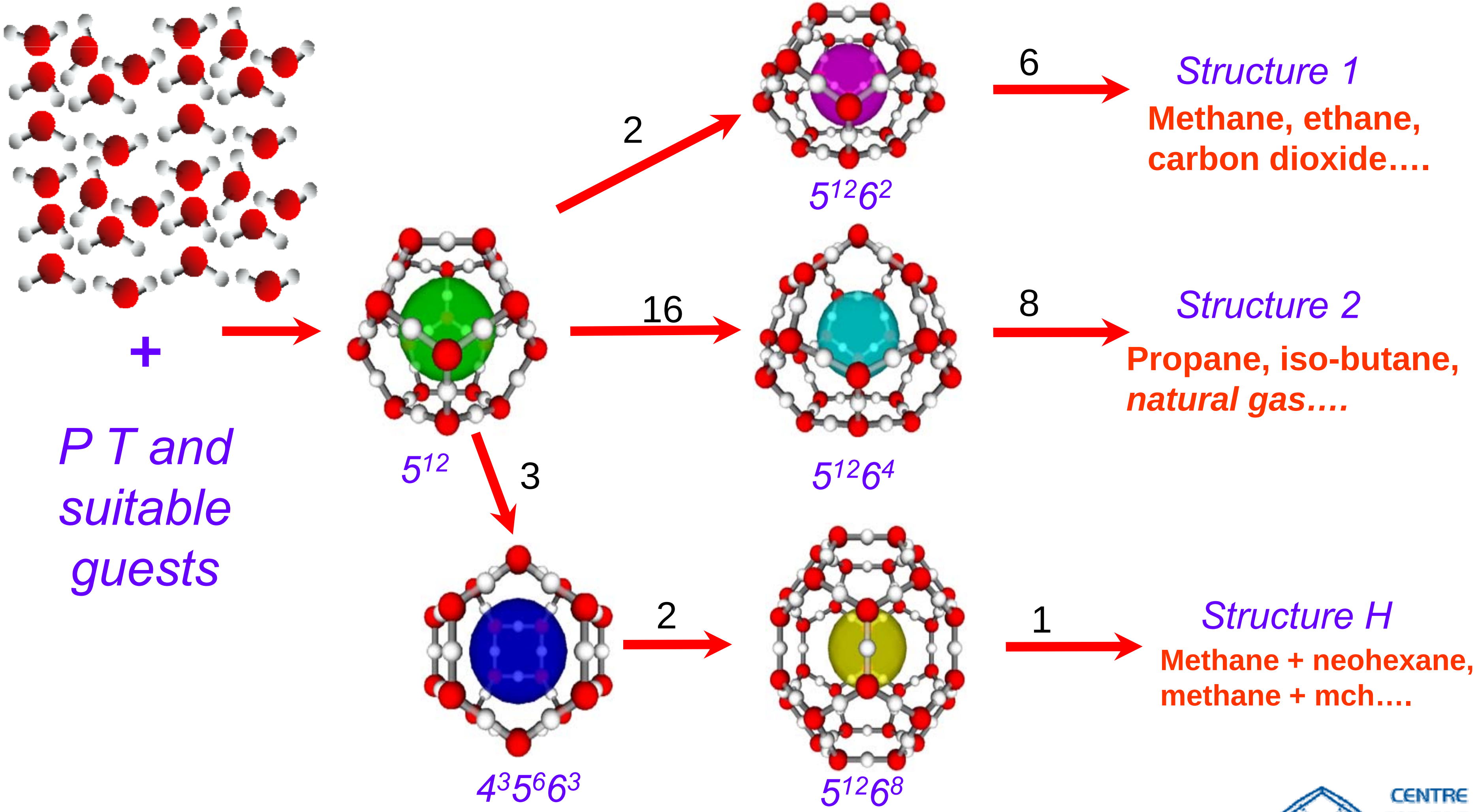
Where Can They Form?

- *They can form anywhere, such as:*
  - Pipelines (offshore and onshore)
  - Processing facilities (separators, valves, etc)
  - Heat exchangers
  - Sediments (permafrost regions and subsea sediments)
  - Offshore drilling operations
  - Etc

Interesting Properties

- *Capture large amounts of gas (up to 15 mole%)*
- *Remove light components from oil and gas*
- *Form at temperatures well above 0 °C*
- *Generally lighter than water*
- *Need relatively large latent heat to decompose*
- *Non-stochiometric*
- *More than 85 mole% water in their structure*
- *Exclude salts and other impurities*
- *Result from physical combination of water and gas*
- *Hydrate composition is different from the HC phase*
- *Large amounts of methane hydrates exist in nature*

Hydrate Structures



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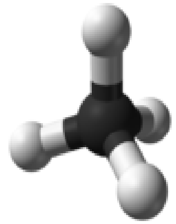
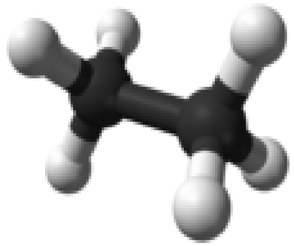
Hydrate former in Natural Gas

- Methane
  - *sI former*
  - *Both small and large cages of SI*



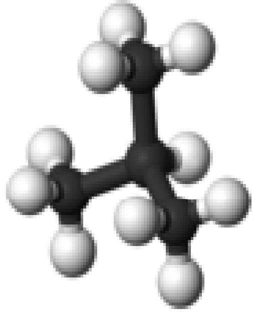
- Ethane
  - *sI former*
  - *Only large cages of SI*

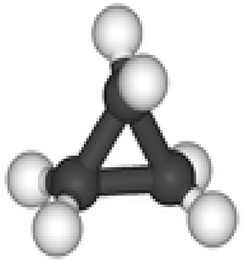


- Propane
  - *sII former*
  - *Only large cages of SII*

Hydrate Formers in Natural Gas

- i-butane
  - *sII former*
  - *Only large cages of sII*
- n-butane
  - *Does not form hydrate on its own*
  - *Form in the presence of another hydrate former, i.e. methane*
  - *Only large cages of sII*
- Cyclo-propane
  - *sI or sII former depending on T and P*
  - *Only large cages*





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Hydrate Formers in Natural Gas: Non Hydrocarbons

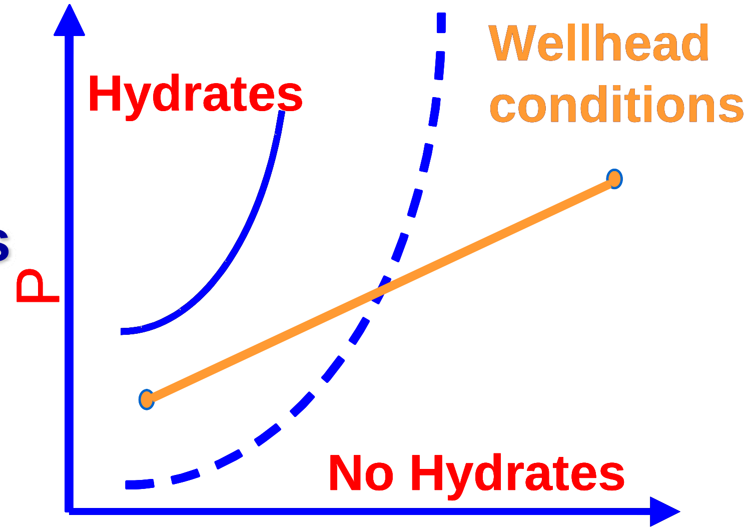
- Nitrogen
  - *sII former*
  - *Small and large cages of sII*
- Carbon dioxide
  - *sI former*
  - *Only large cages of sI*
- Hydrogen Sulphide
  - *sI former*
  - *Small and large cages*

Other Hydrate Formers

- Freons
- Halogens (fluorine and chlorine)
- Noble gases (argon, krypton, xenon, radon *not helium*)
  - *Very stable compound →good indication that no chemical bonding exist between the host and the guest*
- Air (N_2 + O_2)
- SO_2 (very soluble in water) and small mercaptans (methanethiol, ethanthiol and propanethiol)

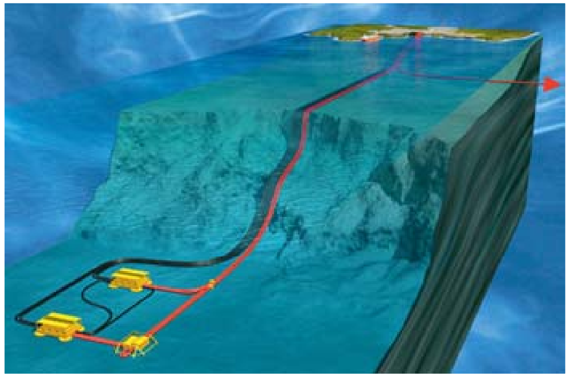
Avoiding Hydrate Problems - Current practice

- Increasing the system temperature
  - Insulation
  - Heating
- Reducing the system pressure
- **Injection of thermodynamic inhibitors**
  - Methanol, ethylene glycol, ethanol
- Using Low Dosage Hydrate Inhibitors
  - Kinetic Inhibitors (KHI)
  - Anti-Aggglomerants (AA)
- **Water removal (dehydratation)**
- Combinations of the above
- New Approach: Cold Flow



Flow Assurance- Hydrates: The problems

- Hydrate blockages are major flow assurance problems in offshore and deep water operations.
- Currently the most common flow assurance strategy is to rely upon injection of inhibitors in order to inhibit hydrate formation.
- It is crucial for accurate knowledge of hydrate phase equilibrium in the presence of inhibitors to avoid gas hydrate formation problems.
- Lack of experimental data, especially for real reservoir fluids.
- Capability to accurately predict the hydrate stability zone is therefore essential to plan potential flow assurance issues.



Gas hydrates removed from a subsea transfer line (Courtesy of Petrobras)

Thermodynamic Modelling

- For VLE or VHE, we have: $f^V = f^L$ or $f^V = f^H$
- CPA EoS:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \rho\frac{\partial \ln(g)}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1 - X^{A_i}\right)$$

$f^V = f^H$

SRK part — Association part

site fractions

$$X^{A_i} = \left(1 + \rho \sum_j \sum_{B_j} x_j X^{B_j} \Delta^{A_i B_j}\right)^{-1}$$

the association strength

$$\Delta^{A_i B_j} = g(d)\left[\exp\left(\frac{\varepsilon^{AB}}{RT}\right) - 1\right]\beta^{A_i B_j} b$$

radial distribution function

$$g(d)^{simp.} = \frac{1}{1 - 1.9\eta}$$

Thermodynamic Modelling

- For Hydrate:

  Solid solution theory of van der Waals and Platteeuw

$$f_w^H = f_w^\beta \exp\left(-\frac{\Delta\mu_w^{\beta-H}}{RT}\right)$$

where

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H = RT\sum_m \bar{v}_m \ln\left(1+\sum_j C_{mj} f_j\right)$$

- Modeling of electrolyte solutions:

  Combining the EoS with the Debye Hückel electrostatic contribution

$$\ln\phi_i = \ln\phi_i^{EoS} + \ln\gamma_i^{EL} \qquad i = 1,2,\dots,n$$

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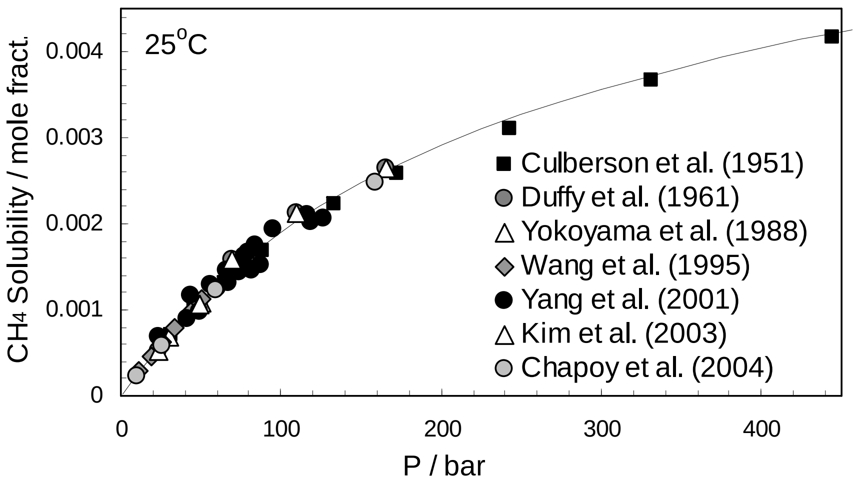
Thermodynamic Modelling

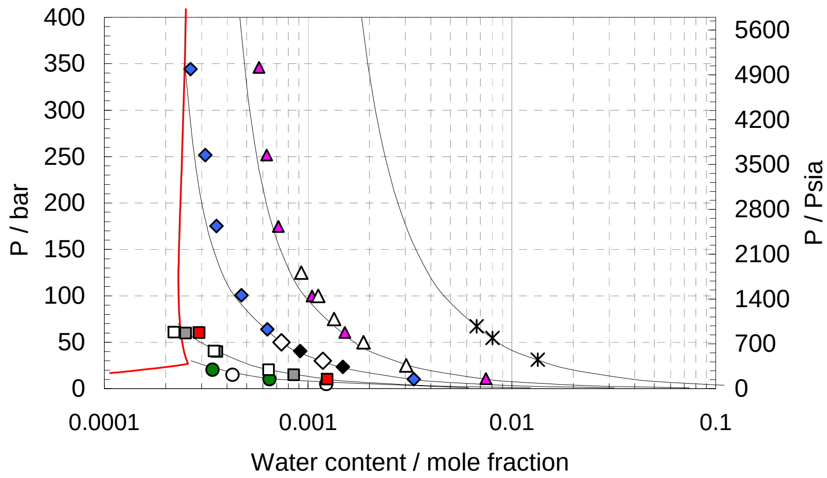
- BIPs between self-associating compounds using solubility data:

$$FOB = \frac{1}{N}\sum_{1}^{n}\left|\frac{x_{i,\exp} - x_{i,cal}}{x_{i,\exp}}\right|$$

- methane-water:



Solubility of methane in water at 25 °C.



Water content of methane in equilibrium with liquid water 0, 10, 25, 40 and 75°C.

Haghighi H., Chapoy A., Tohidi B., 2009, J. Oil Gas Sci. Technol., 64, 141.

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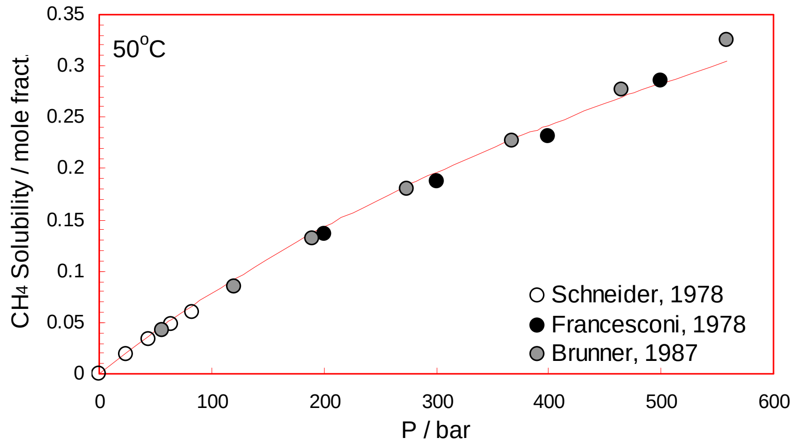
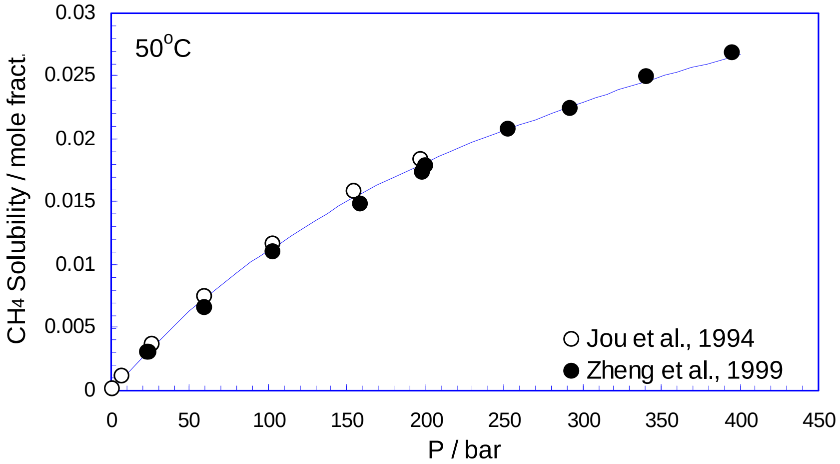
Thermodynamic Modelling

- methane-methanol:

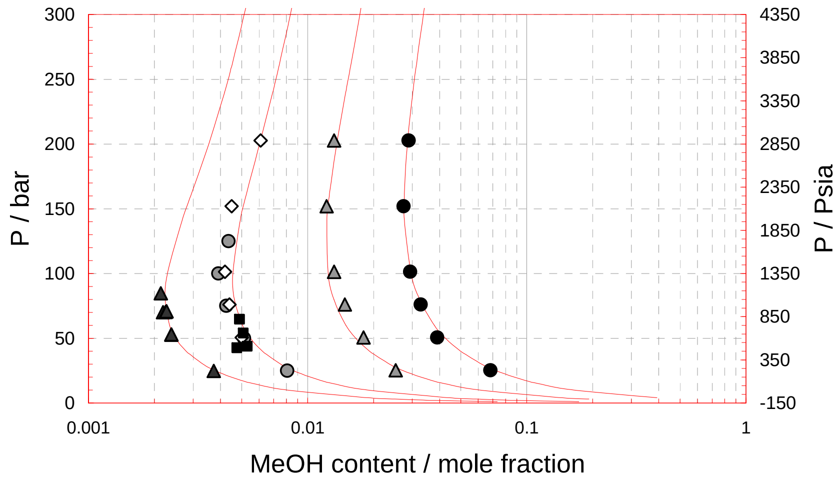


Solubility of methane in methanol at 50 °C.

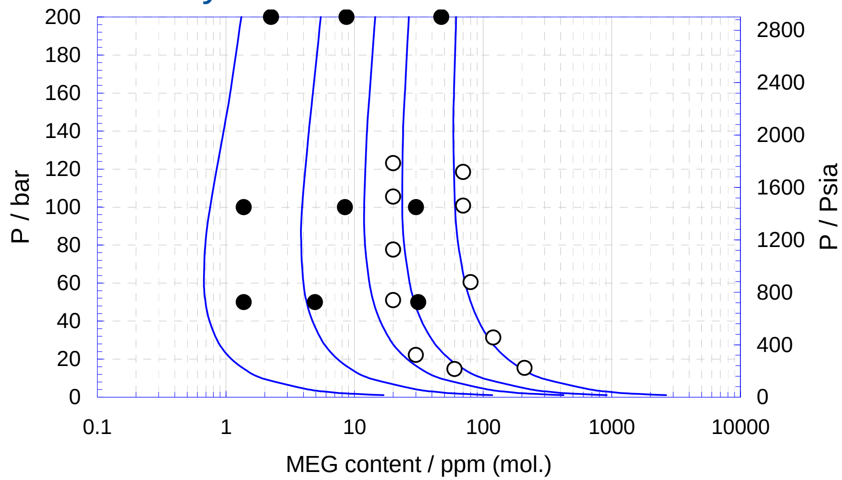
- methane-MEG:



Solubility of methane in MEG at 50 °C.



Water content of methane in equilibrium with liquid methanol 10, 25, 50 and 75°C.



Water content of methane in equilibrium with liquid MEG 5, 10, 40, 50 and 65°C.

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Thermodynamic Modelling

- BIPs between cross-associating compounds (e.g. water-methanol and water-MEG) adjusted using VLE (bubble and dew point data) or SLE (freezing point depression data) :

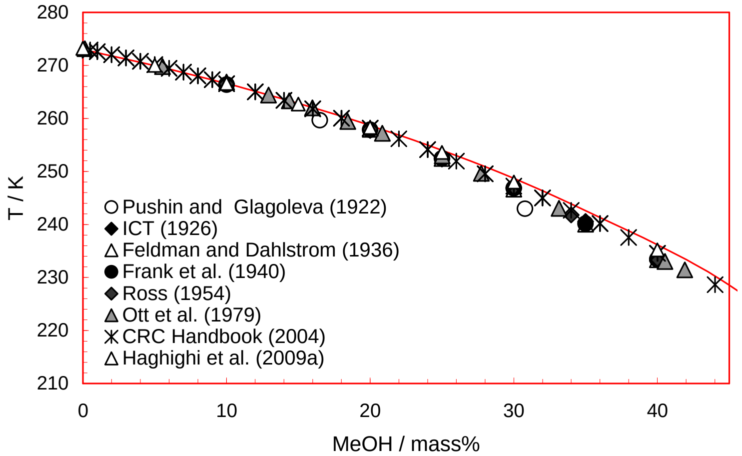
Objective Function:

$$FOB = \frac{1}{N}\sum_{1}^{n}\left|\frac{x_{i,\exp} - x_{i,cal}}{x_{i,\exp}}\right| \quad \text{For SLE data}$$

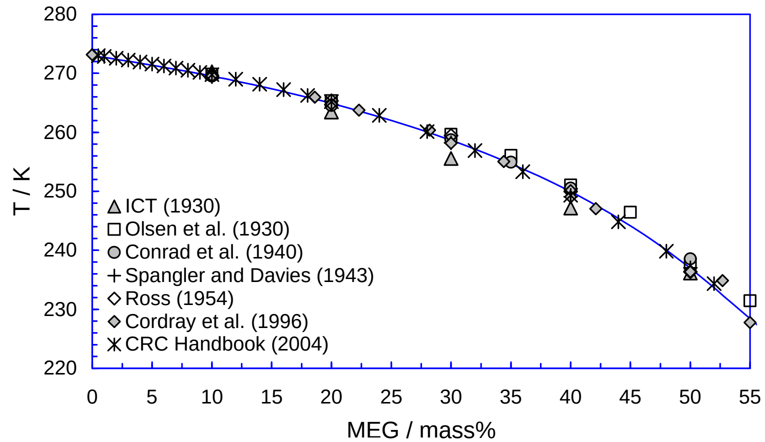
$$FOB = \frac{1}{N}\sum_{1}^{n}\left|\frac{T_{i,\exp} - T_{i,calc}}{T_{i,\exp}}\right| \quad \text{For VLE data}$$

Thermodynamic Modelling

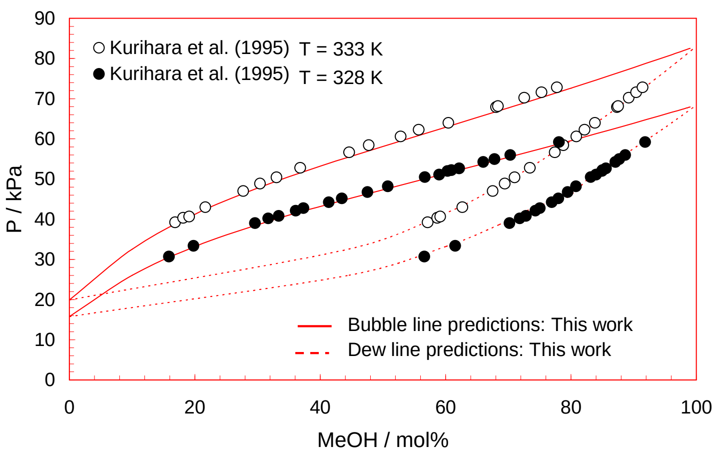
- SLE for water-methanol:



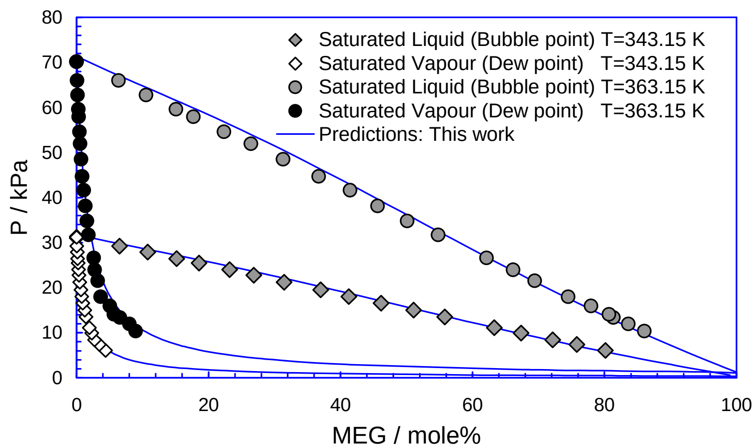
- SLE for water-MEG:



- VLE for water-methanol:



- VLE for water-MEG:



Haghighi H., Chapoy A., Burgess R., Mazloum S., Tohidi B., 2009, J. Fluid Phase Equilibr., 278, 109-116.

Haghighi H., Chapoy A., Tohidi B., 2009, J. Fluid Phase Equilibr., 276, 24-30.

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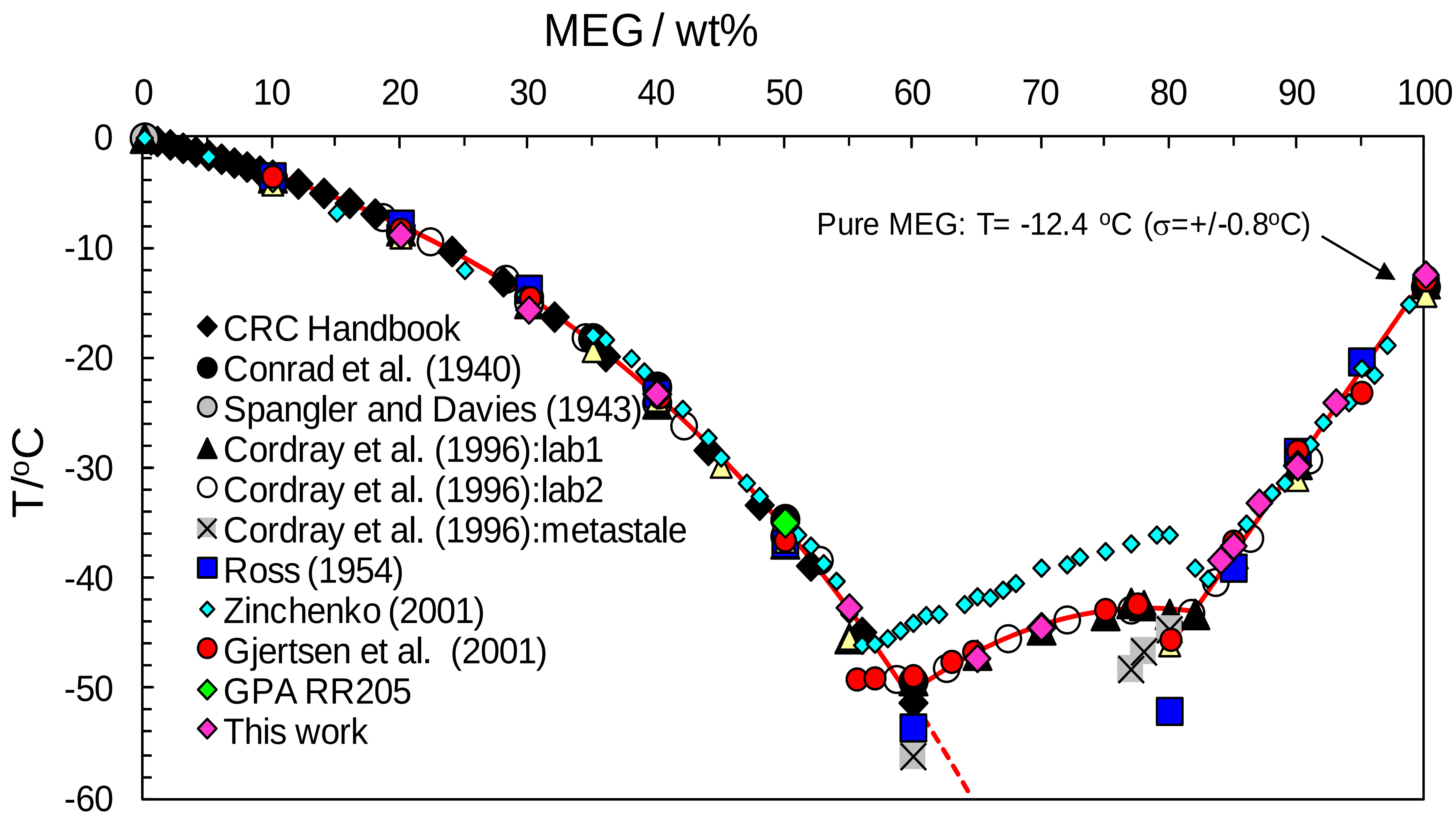
Thermodynamic Modelling

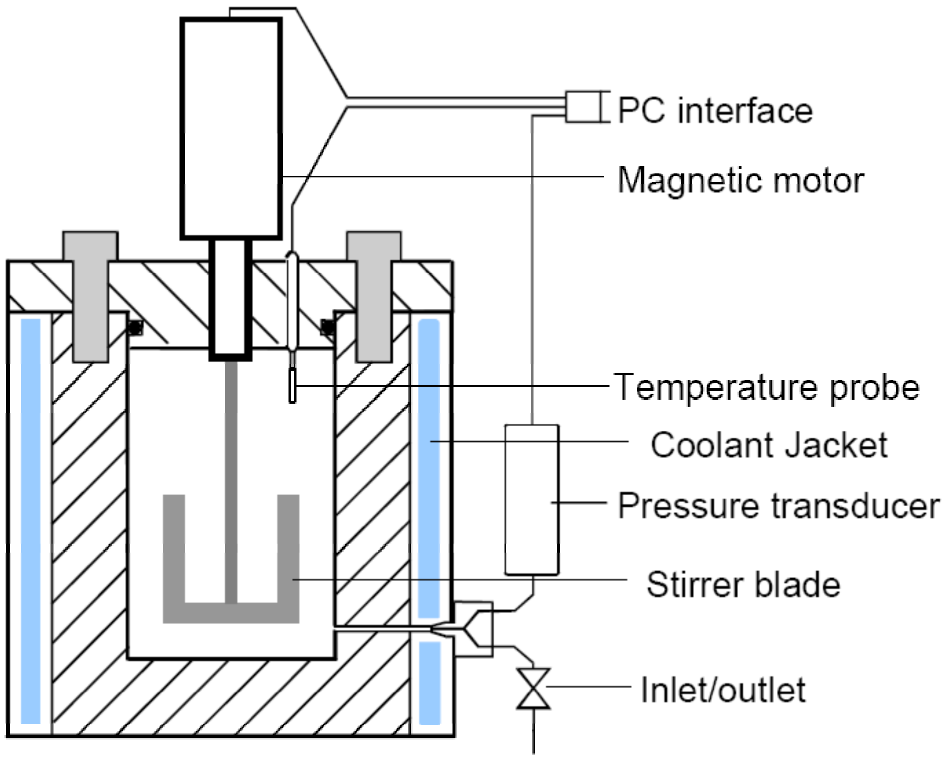


Avoiding Hydrate Problems - Current practice

- Increasing the system temperature
  - *Insulation*
  - *Heating*
- Reducing the system pressure
- **Injection of thermodynamic inhibitors**
  - ***Methanol, ethylene glycol, ethanol***
- Using Low Dosage Hydrate Inhibitors
  - *Kinetic Inhibitors (KHI)*
  - *Anti-Aggglomerants (AA)*
- Water removal (dehydratation)
- Combinations of the above
- New Approach: Cold Flow

Experimental Equipment

- Materials:
  - *Distilled water*
  - *North Sea natural gas*
  - *Inhibitors*
- Equipments:
  - *Autoclave cells*
  - V = *300 to 2000 ml*
  - *Max* P = *400 – 2000 ba*
  - *-80 < T < 50 °C*



Typical Experimental Procedures

- Cell loaded with starting fluids at *T* = 20 °C or higher
  - *Depending on experiment: water ± salts ± Thermodynamic inhibitor (MEG, methanol)*
  - *Headspace left for further fluid injections: gas (G), live oil…*
- To form hydrates, temperature reduced, their presence being confirmed by pressure drop
- Hydrate dissociation point is found by stepwise increase of T

Hydrates: Experimental Methods