New Apparatus For Solid-Fluid Equilibrium Measurements

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Introduction

- The production of LNG requires temperatures as low as - 161 °C (-112 K), which is the normal boiling point of methane.

<u>Current LNG specifications</u>

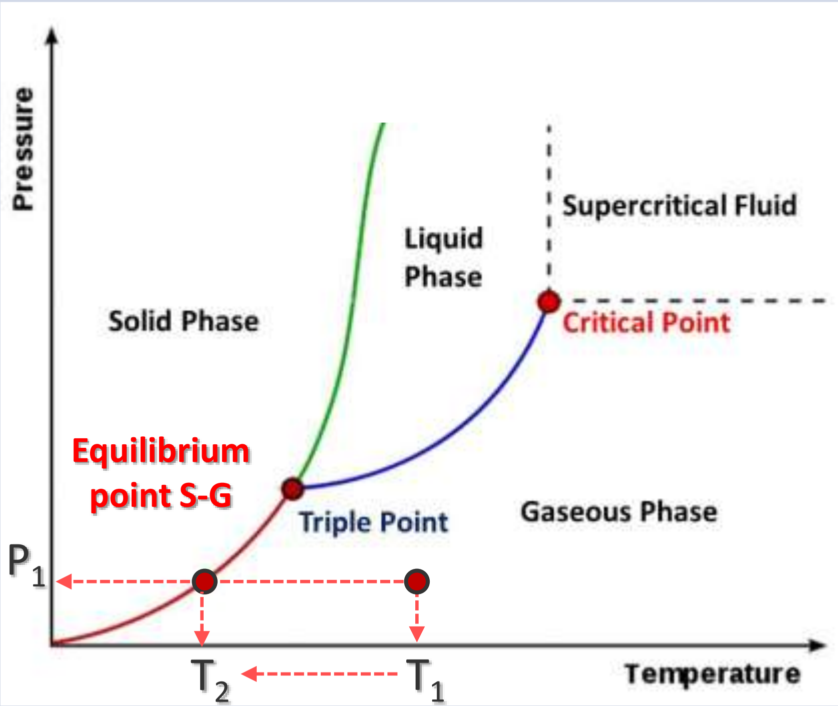
CO_2 < 50 ppm
Water < 0.1 ppm
C4 ≤ 2 mol%
C5+ ≤ 0.1 mol%
Aromatics < 2 ppm

} Very low allowable impurity levels in the gas

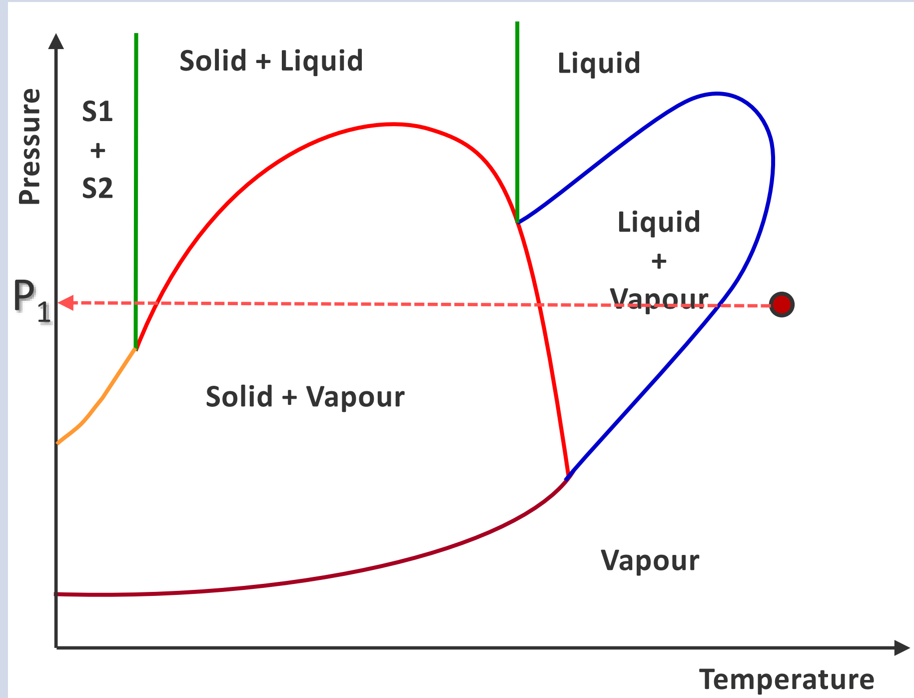
- **It is necessary to avoid solids deposition that can plug the different parts of equipment in the liquefaction chain (heat exchangers).**

- **The objective is to investigate whether the existing specifications are reflecting the actual freeze out conditions, in order to identify if there is a potential for larger margins towards freeze out in the liquefaction process.**

Fluid phase equilibrium



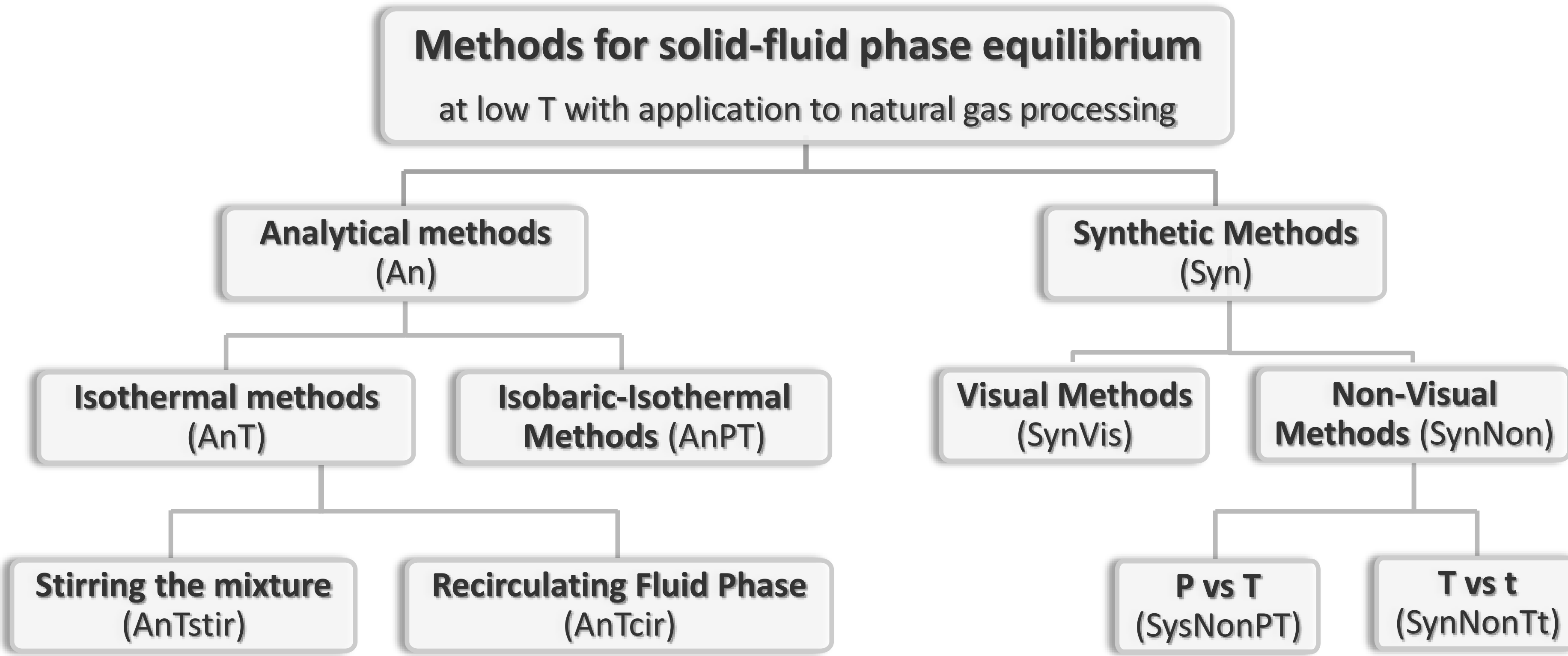
Pure component



Binary mixture

Figure adapted from Donnelly, H. G. and Katz, D. L., Ind. Eng. Chem. 1954, Vol. 46 (3), 511-517

Methodology in the field of solid-fluid measurements



Reference: L. Zhang, *Solid-fluid phase equilibria for natural gas processing at low temperatures*, Ph.D., in: Department of Energy and Process Engineering, Norwegian University of Science and Technology, Trondheim, 2012.

Freeze-out apparatus

Innovation

both analytical and synthetic methods can be combined for measurements

Custom made for Statoil by Sanchez technologies, was further developed internally.

Main elements of the rig

- Double envelope container
- Sapphire cell with stirrer and cold finger
- Two pumps for fluid circulation
- Sampling system with ROLSI® valves
- Falkon software for control and data acquisition

Specifications

Temperature range: -170 – (+40)^{o}C

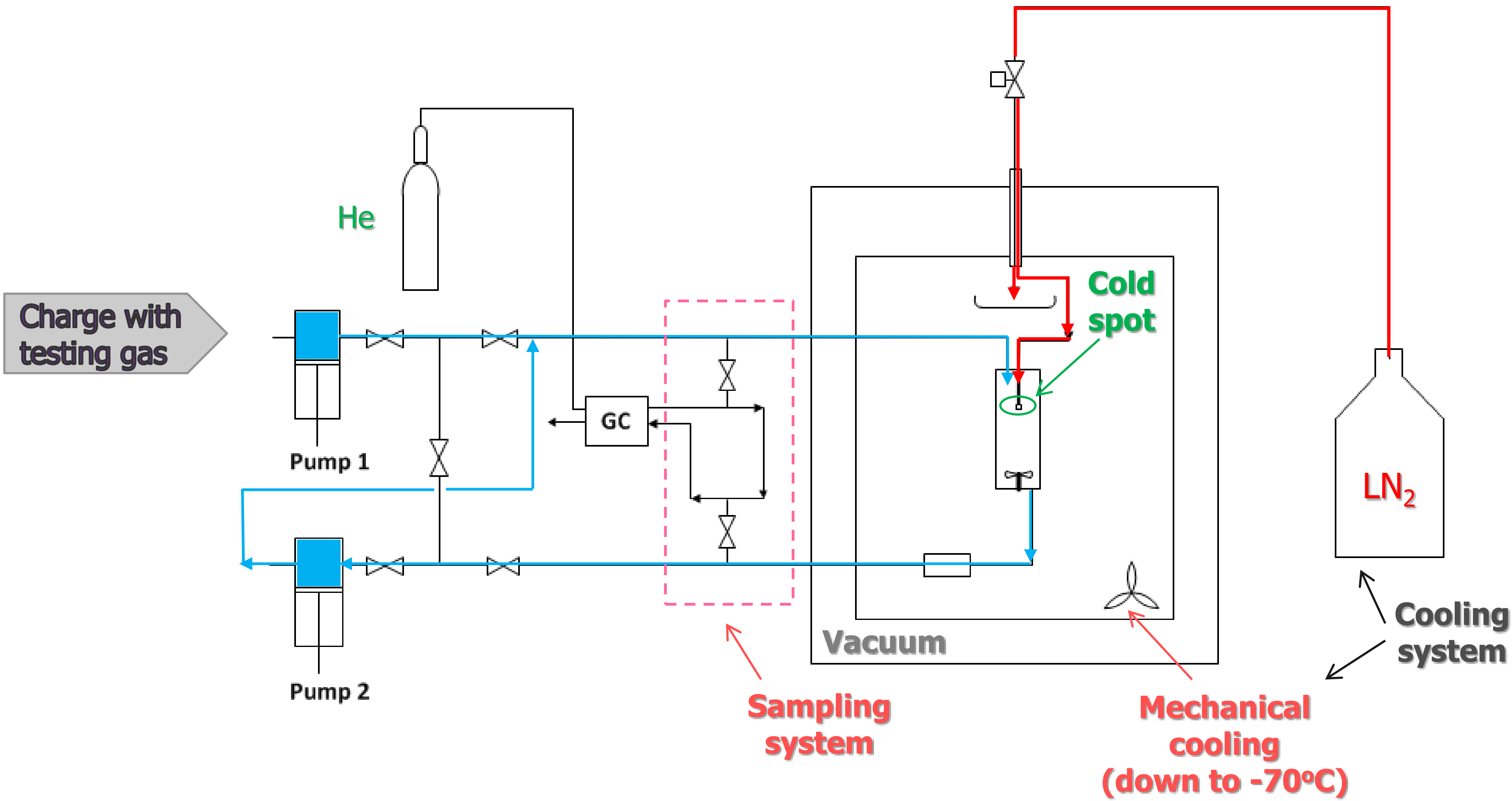
Pressure range: vacuum to 500bar

Sapphire cell volume: 80mL

Cell plus piping volume: 170mL

Principle of Operation

1. Synthetic method ⟹ e.g. keep P const and cool down until solids form
2. Analytical method ⟹ Set P, cool down + recirculate + stirring until solids are form.



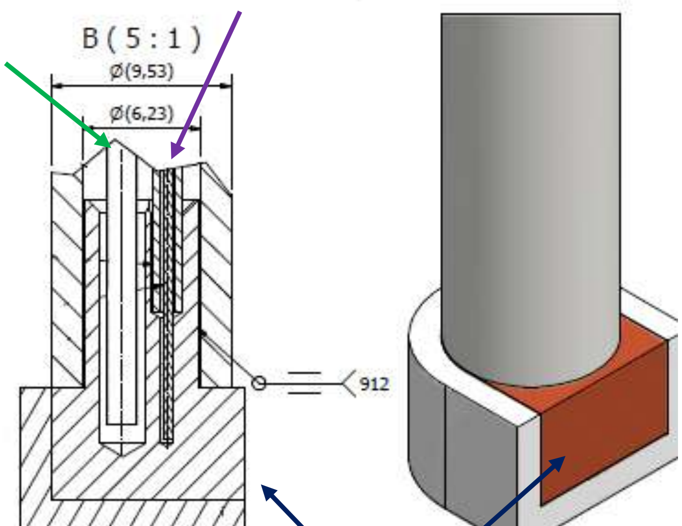
Detection method

Solids are visually detected on the cold-finger

PT100 thermo-component

LN_2 inlet

thermocouple



56 mm²

Solid deposition

Thermodynamic Model

At equilibrium:

$$\begin{cases} P^{\alpha} = P^{\beta} \\ T^{\alpha} = T^{\beta} \\ f_i^{\alpha} = f_i^{\beta} \end{cases}$$

α, β are different phases,
i is the component

Fluid phase

SRK EoS: $P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$

with
vdWaals mixing rule

$$a = 0.42748\frac{(RT_c)^2}{P_c}\left[1 + m\left(1 - \left(\frac{T}{T_c}\right)^{0.5}\right)\right]^2$$

$$m = 0.48 + 1.57\omega - 0.176\omega^2$$

$$b = 0.08664\frac{RT_c}{P_c}$$

$$ln\frac{f_i^a}{x_i P} = \frac{B_i}{B}(z-1) - ln(z-B) - \frac{A}{B}\left(\frac{2\sum x_j A_{ij}}{A} - \frac{B_i}{B}\right) ln\left(1 + \frac{B}{z}\right)$$

Solid phase

based on the assumption of the existence of a sub-cooled liquid at the same T, P as the solid:

$$ln\left(\frac{f_i^L}{f_i^S}\right) = \frac{\Delta H_{fus}}{RT_t}\left(\frac{T_t}{T} - 1\right) - \frac{\Delta C_P}{R}\left(\frac{T_t}{T} - 1\right) + \frac{\Delta C_P}{R} ln\frac{T_t}{T}$$

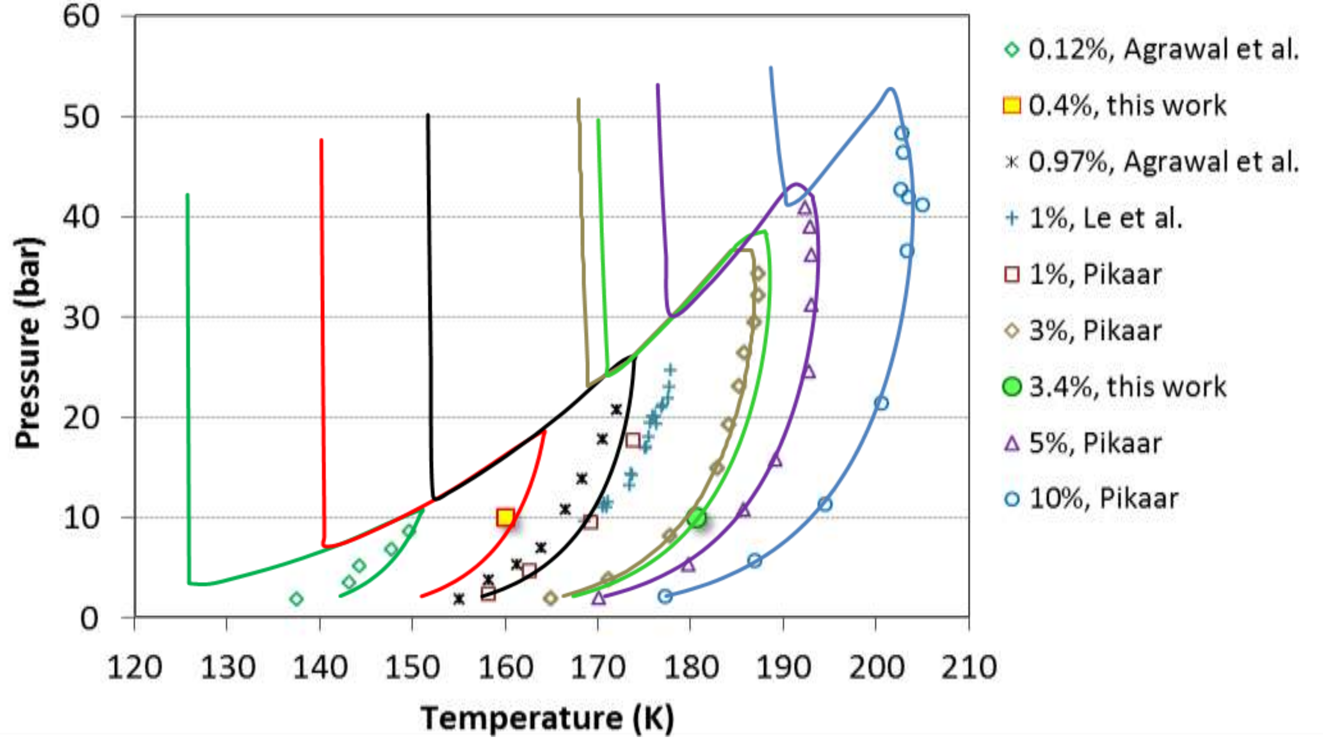
Enthalpy of fusion

Heat capacity difference

Triple point temperature

Results

- Measurements were performed for CO_2/CH_4 mixtures and compared to available literature data



- Two frost points, comparable to the literature experimental data.
- Satisfactory predictions in the solid-vapor range.

Conclusions

- ✓ The experimental apparatus can successfully be used for solid-vapor equilibrium meauserements.
- ✓ Further work on the solid-liquid equilibrium and the SLV should be performed so as to verify the overall capabilities of the apparatus.
- ✓ Satisfactory predictions in the solid-vapor range with the SRK EoS.

There's never been a better time for good ideas

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