# New data & improved models of the solubility of sulphur compounds in liquefied natural gas

Professor Eric F. May

University of Western Australia (UWA)

Future Energy Exports CRC

# Acknowledgements


**Co-authors**

Mark Barwood (UWA)

Rossen Sedev (UWA)

Paul Stanwix (UWA)

Peter Falloon (UWA)

Xiong Xiao (UWA)

Brendan Graham (UWA)

Robert Marriott (U Calgary)

**Project 213 Coordinators**

Oliver Koch (Linde)

Dale Embry (ConocoPhillips)

**Project Funding**

GPA MIDSTREAM ASSOCIATION

FUTURE ENERGY EXPORTS Cooperative Research Centre

# Project 213 Background

IMPURE NATURAL GAS → IMPURITY REMOVAL → CLEANED GAS →

→ LNG

$H_2O$, BTEX, $CO_2$, $C_{6+}$ (well-studied)
Sulphur compounds (e.g. $H_2S$)

There are few data available for sulphur compounds

- Ubiquitous contaminants – from reservoir ($H_2S$) or odorants
- Difficult to tune thermodynamic models
- Challenging to assess freeze-out risk associated with contaminants

# Project 213 Objectives

1. Collect literature data & implement models in free *ThermoFAST* software to predict solubility of 19 S-containing compounds in LNG
2. Construct a sulphur-compatible apparatus to measure S-compound freeze-out from methane
3. Measure $H_2S$, COS, methanethiol (MeSH) & ethanethiol (EtSH) solubility in $CH_4$ at (100-140) K [-280 to -207 F] & pressures to 5 MPa [725 psia]
4. Tune interaction parameters for these four binary mixtures to improve *ThermoFAST's* solubility predictions to within 0.5 K [0.9 F]
5. Establish new methods of predicting solid solubility of impurities in LNG that are more accurate, or need less data, than the current approach

# Priority Sulphur-Containing Compounds

| Compound Name | CAS | Formula | Priority | $T_t$ [K] | Crystals | Measured |
|---|---|---|---|---|---|---|
| *tert*-Butanethiol | 75-66-1 | $C_4H_9SH$ | 1 | 274.42 | 3 (4) | No |
| Hydrogen Sulphide | 7783-06-4 | $H_2S$ | 1 | 190.9 | 3 | Yes |
| *n*-Propanethiol | 107-03-9 | $C_3H_7SH$ | 1 | 160 | 2 | No |
| Methanethiol (MeSH) | 74-93-1 | $CH_3SH$ | 1 | 150.1 | 2 | Yes |
| Ethanethiol (EtSH) | 75-08-1 | $C_2H_5SH$ | 1 | 125.2 | 1 | Yes |
| Diethyl Sulphide | 352-93-2 | $C_2H_5SC_2H_5$ | 1 | 169.2 | 1 | No |
| Tetrahydrothiophene | 110-01-0 | $C_4H_8S$ | 2 | 176.98 | 2 | No |
| Dimethyl disulphide | 624-92-0 | $CH_3SSCH_3$ | 2 | 188 | 1 | No |
| Dihydrogen disulphide | 13465-07-1 | $H_2S_2$ | 2 | 183.6 | 1 | No |
| Dimethyl sulphide | 75-18-3 | $CH_3SCH_3$ | 2 | 174.9 | 1 | No |
| Ethyl methyl sulphide | 624-89-5 | $C_2H_5SCH_3$ | 2 | 167.2 | 1 | No |
| Carbon disulphide | 75-15-0 | $CS_2$ | 2 | 161.1 | 1 | No |
| *n*-Butanethiol | 109-79-5 | $C_4H_9SH$ | 2 | 157.47 | 1 | No |
| 2-Butanethiol | 513-53-1 | $C_4H_9SH$ | 2 | 133.01 | 1 | No |
| *iso*-Propanethiol | 75-33-2 | $C_3H_7SH$ | 3 | 142.6 | 2 | No |
| *iso*-Propyl methyl sulphide | 1551-21-9 | $C_3H_7SCH_3$ | 3 | 171.65 | 1 | No |
| Carbonyl Sulphide | 463-58-1 | COS | 3 | 134.3 | 1 | Yes |
| Sulphur Dioxide | 7446-09-5 | $SO_2$ | 3 | 197.64 | 1 | No |
| *iso*-Butanethiol | 513-44-0 | $C_4H_9SH$ | 3 | 133 | 1 | No |

Availability and solubility in $CH_4$ were practical considerations

# Calculating Solid Solubility in LNG

Two thermodynamic models needed to calculate solubility

One for fluid mixture (e.g. $H_2S + CH_4$):

**Peng-Robinson EOS**

→ Interaction parameter, $k_{ij}$

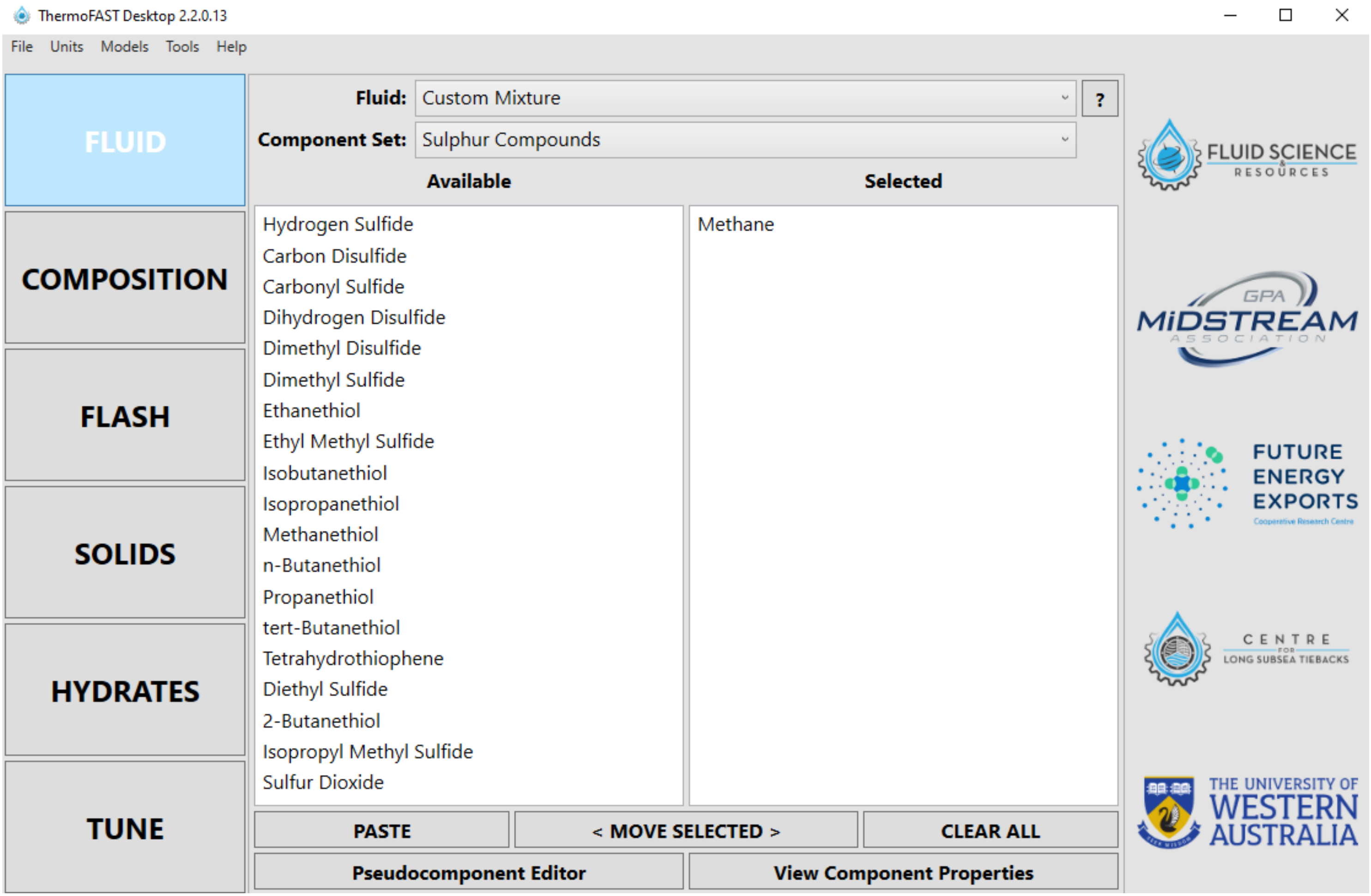
One for pure solid (e.g. $H_2S$):

**i) Classical method**

→ Pure substance properties

$\Delta H_f, \ \Delta c_p^{F\rightarrow S}, \ \Delta v^{F\rightarrow S}$

**ii) EOS for pure solid** (new approach)




Models implemented in free software *ThermoFAST*

# Parameters for predicting solids solubility

Initial parameters taken from literature data

Some pure compounds have solid crystal phase transitions at temperatures down to LNG conditions: these are included

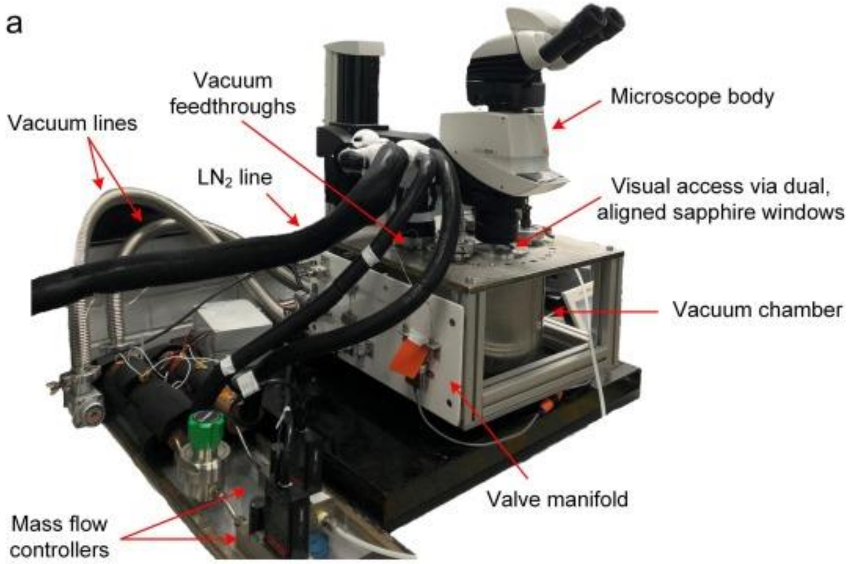
Parameters for 4 compounds then updated based on solubility measurements

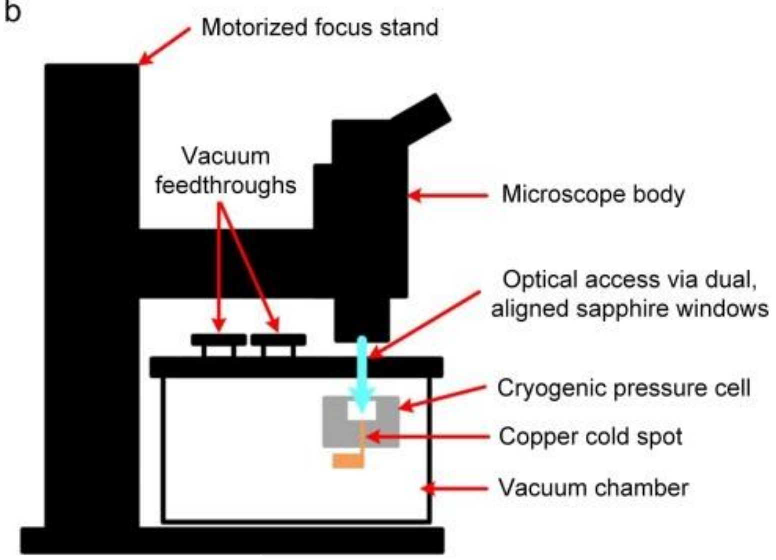
| Compound | $T_t$ [K] | $\Delta H_{fus}$ [J/mol] | $\Delta c_{P,i}^{F\rightarrow S}$ [J/mol/K] | $\Delta v_i^{F\rightarrow S}$ [cm³/mol] |
|---|---|---|---|---|
| *tert*-Butanethiol | 274.4 | 2481.9 | -317.1 | 15.7 |
| Hydrogen Sulphide | 190.9 | 2375 | -10 | 2 |
| *n*-Propanethiol | 160.0 | 5476.9 | 46.4 | 11.5 |
| Methanethiol | 150.1 | 5905.3 | -72.2 | 6.69 |
| Ethanethiol | 125.2 | 4974.8 | 45.7 | 8.94 |
| Diethyl Sulphide | 169.2 | 11903.5 | 54.3 | 0 |
| Tetrahydrothiophene | 176.9 | 7352.1 | 81.6 | 15.0 |
| Dimethyl disulphide | 188.0 | 9192.2 | 85.1 | 1.6 |
| Dihydrogen disulphide | 183.6 | 7555.6 | 60.3 | 1.12 |
| Dimethyl sulphide | 174.9 | 8286 | 57.8 | 1.06 |
| Ethyl methyl sulphide | 167.2 | 9761.3 | 42.4 | 11.4 |
| Carbon disulphide | 161.1 | 4389 | 16 | 3.48 |
| *n*-Butanethiol | 157.4 | 10460 | 60.4 | 13.8 |
| 2-Butanethiol | 133.0 | 6477 | 69.5 | 0 |
| *iso*-Propanethiol | 142.6 | 5736.3 | 17.0 | 11.7 |
| *iso*-Propyl methyl sulphide | 171.6 | 9360 | 0 | 0 |
| Carbonyl Sulphide | 134.3 | 4727 | 8.05 | 1.07 |
| Sulphur Dioxide | 197.6 | 2063 | 17.8 | 0 |
| *iso*-Butanethiol | 133.0 | 4982.3 | 61.6 | 13.4 |

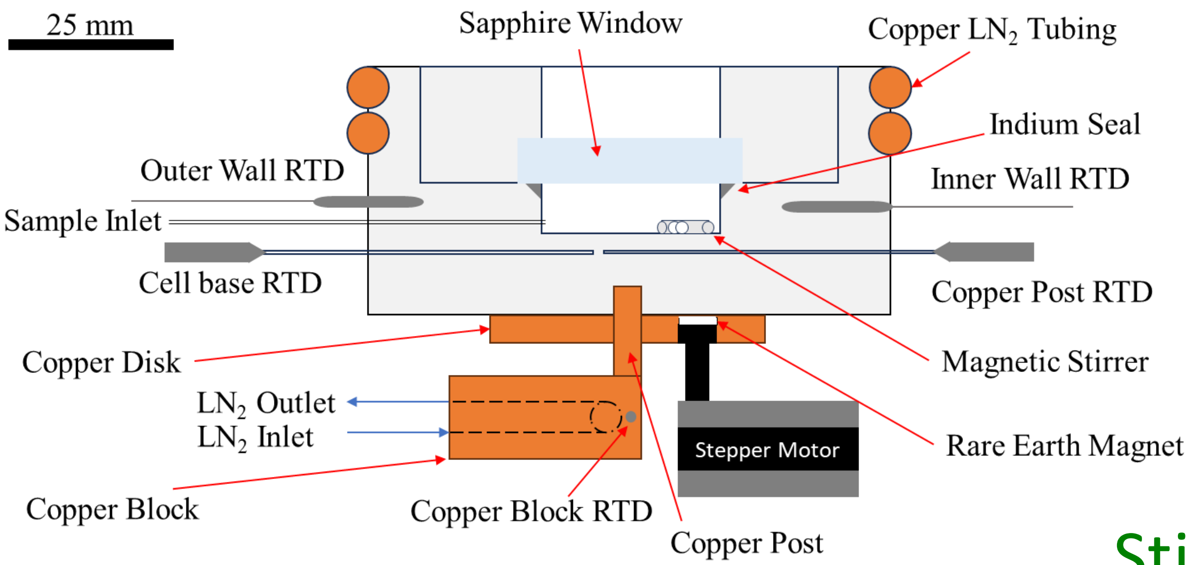
# Cryoscope Apparatus

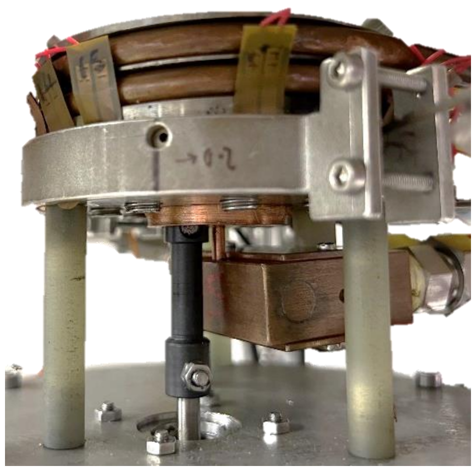
# Optical Measurements of Solid Solubility

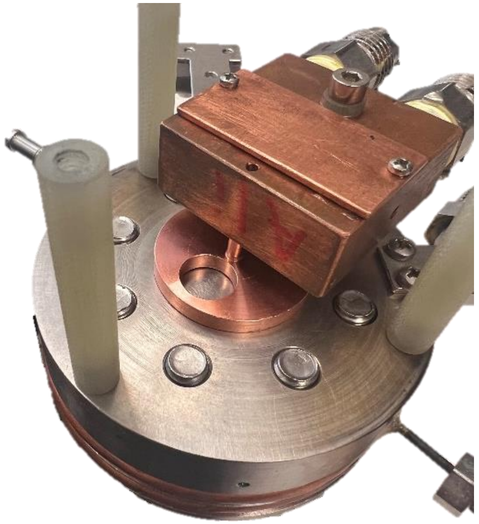
"**Cryoscope**": Cryogenic Microscopy



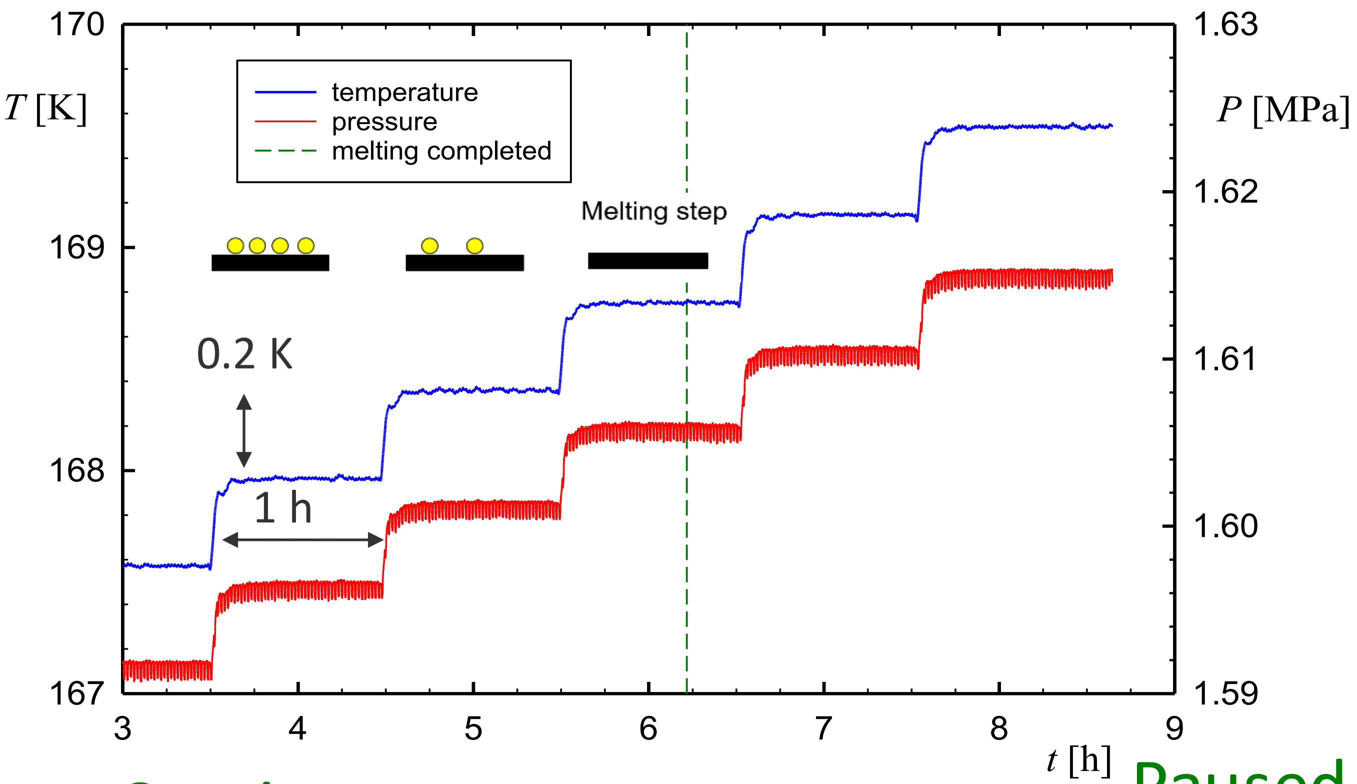





Stir bar driven by stepper motor

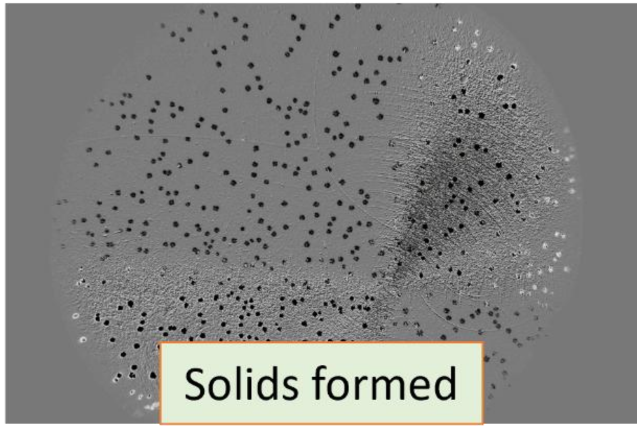
# Optical Measurements of Solid Solubility

Operating range: $T > 90$ K, $p < 20$ MPa

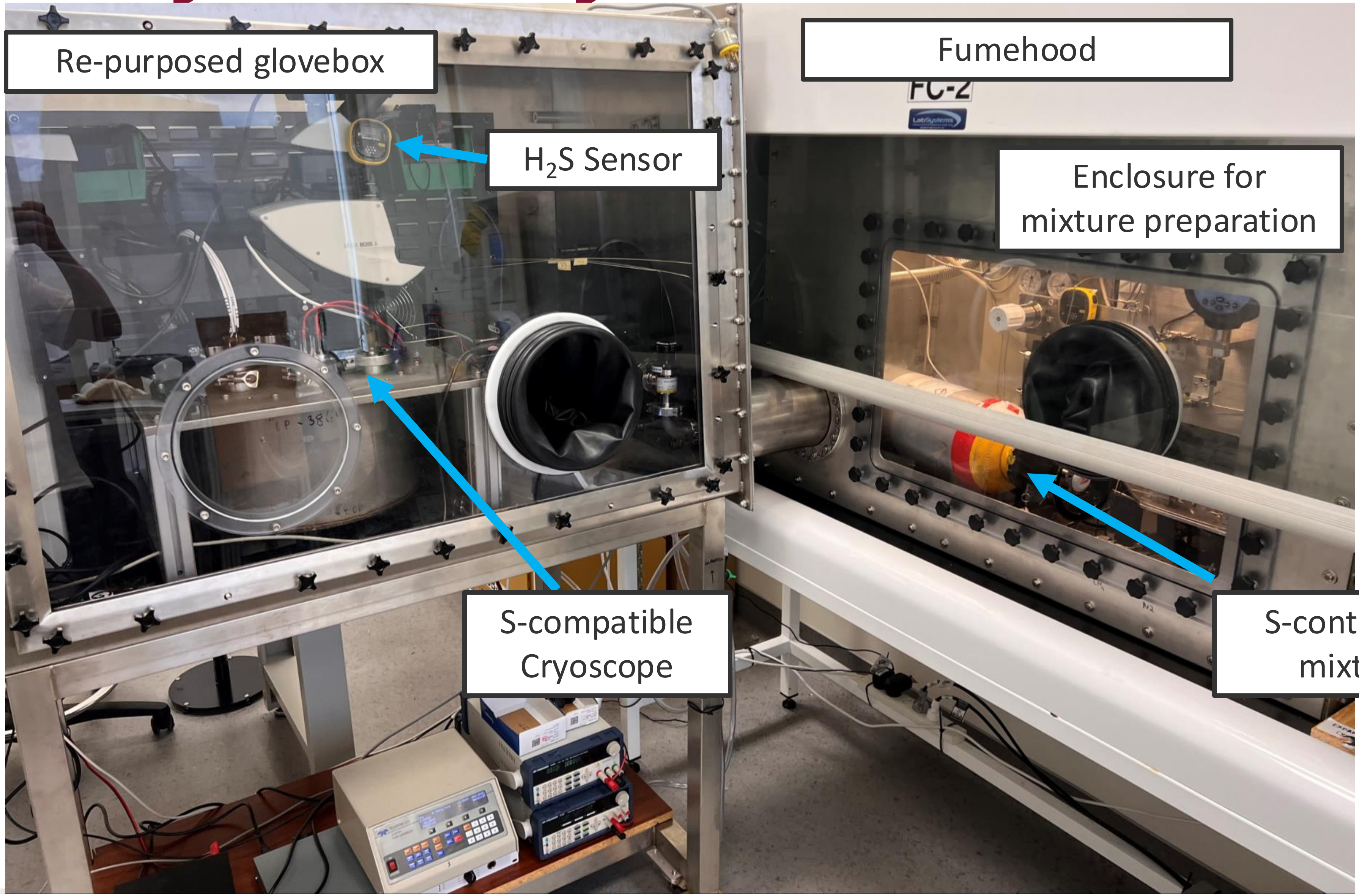


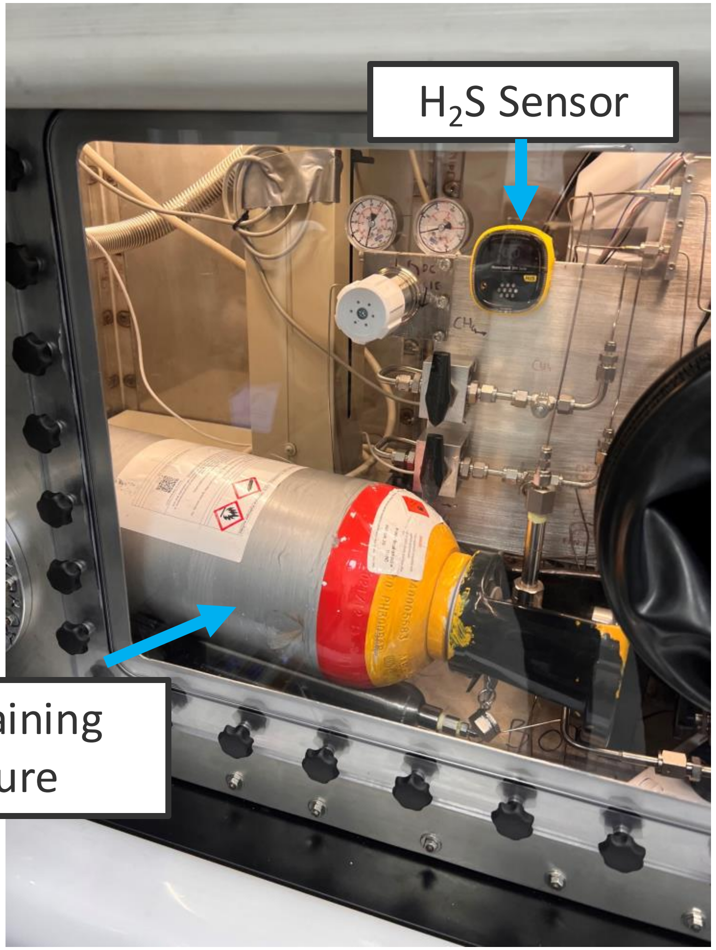

Continuous pulse stirring

Paused for images




# System Layout

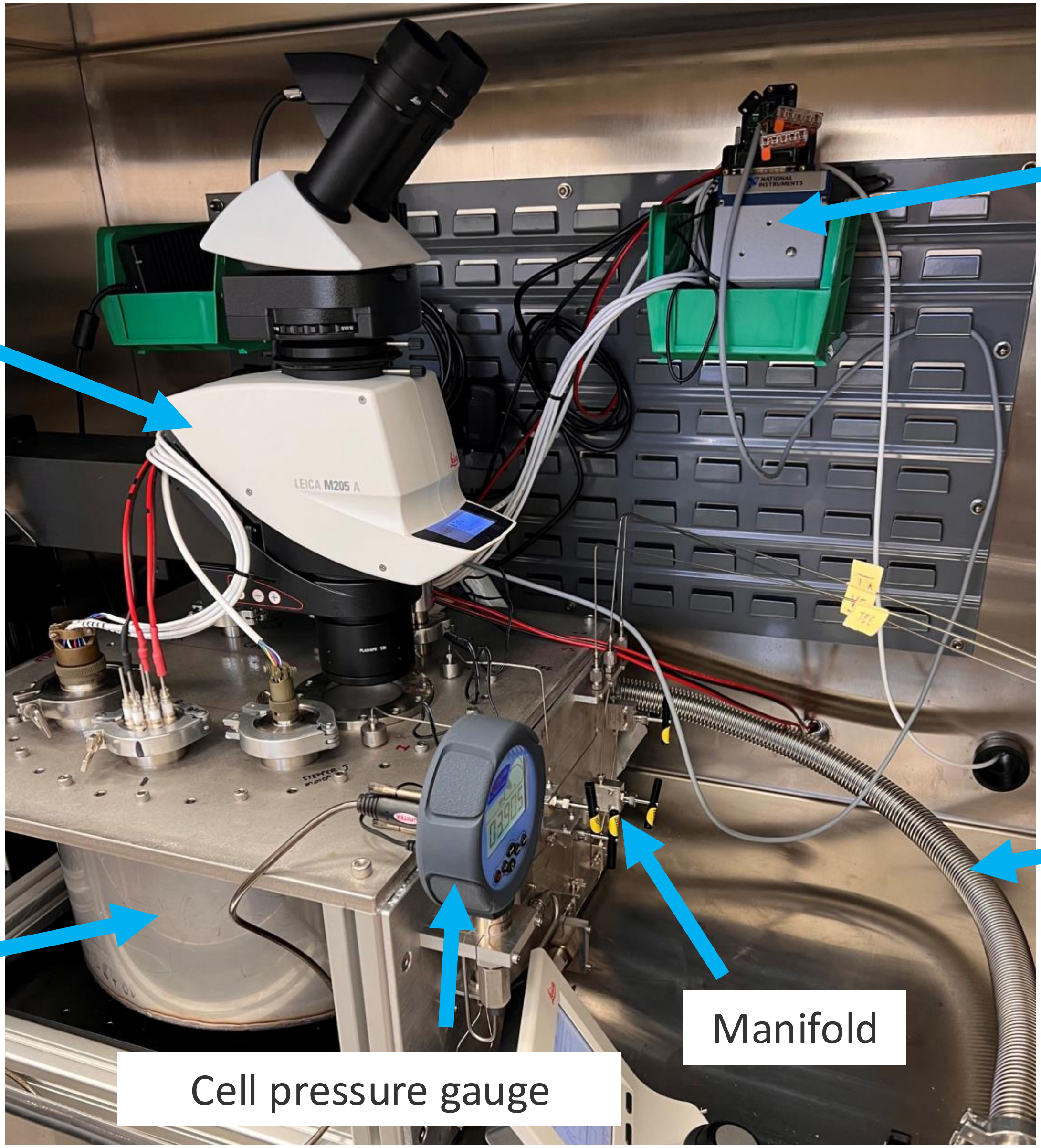


# Measurement system inside glovebox

Data acquisition

Stereomicroscope




Vacuum line

Vacuum chamber

# Robust Safety Measures in Place

Both the glovebox and enclosure are air-tight

- Can be purged with compressed air (sent to scrubbing)
- All vent lines also sent to scrubbing

Scrubbing: NaOH solution (2 M), bleach (14% active Cl)

- Converts S-compound to $SO_4^{2-}$ ions

$H_2S$-specific measures

- 1 room gas sensor and 4 portable sensors
- Full-face mask with protection factor of 1000
- Measurements complete with no safety incidents

# Solubility Measurements

# Synthetic binary mixtures

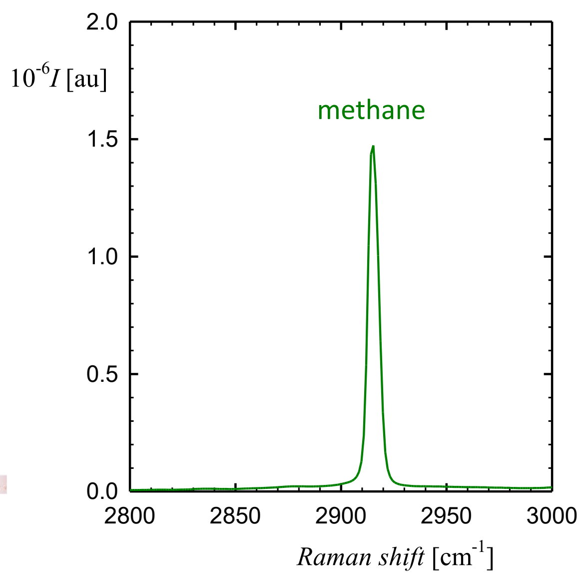
Measurements made using synthetic method. Constant composition

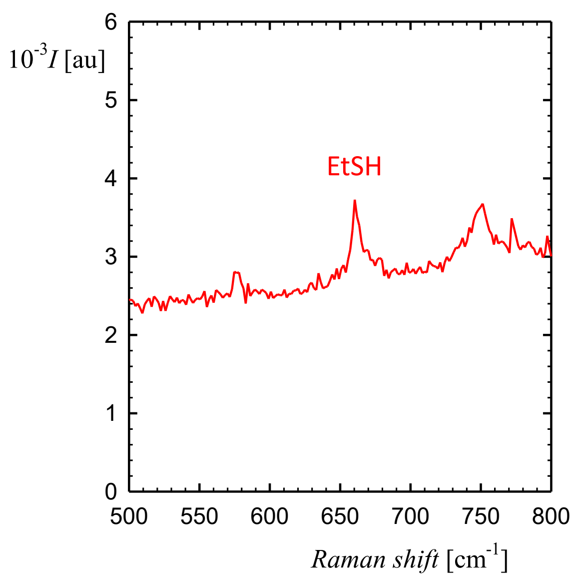
Four certified binary gas mixtures purchased

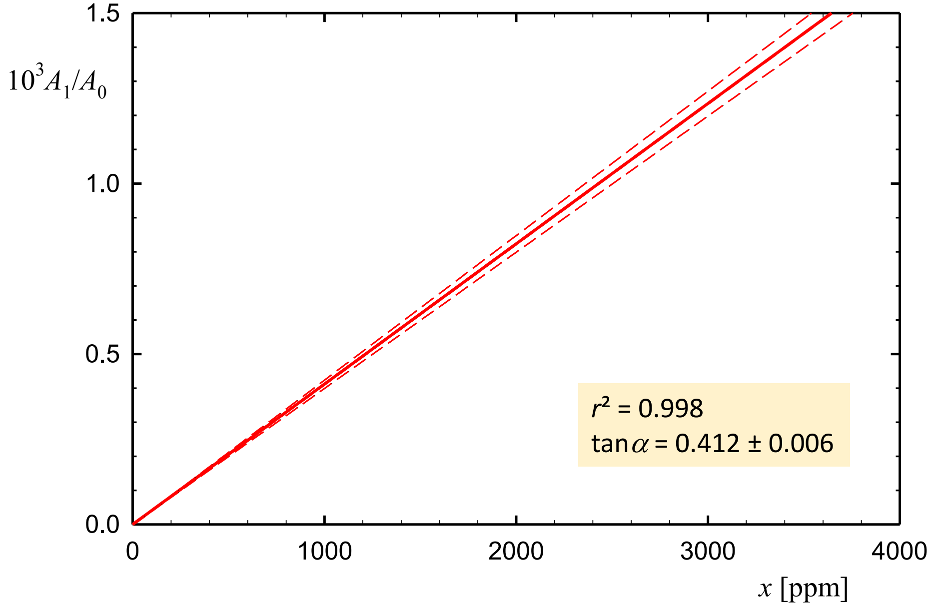
| Compound in $CH_4$ | Formula | $x$ [ppm] | $u(x)$ [ppm] | $u_r(x)$ [%] |
|---|---|---|---|---|
| Hydrogen Sulphide | $H_2S$ | 4,900 | 50 | 1.0 |
| Carbonyl Sulphide | COS | 49,400 | 200 | 0.4 |
| Methanethiol (MeSH) | $CH_3SH$ | 967 | 13 | 1.3 |
| Ethanethiol (EtSH) | $C_2H_5SH$ | 3,040 | 30 | 1.0 |

Each binary measured at 3 concentrations, achieved by dilution with pure $CH_4$

Composition from dilution checked independently with Raman spectroscopy



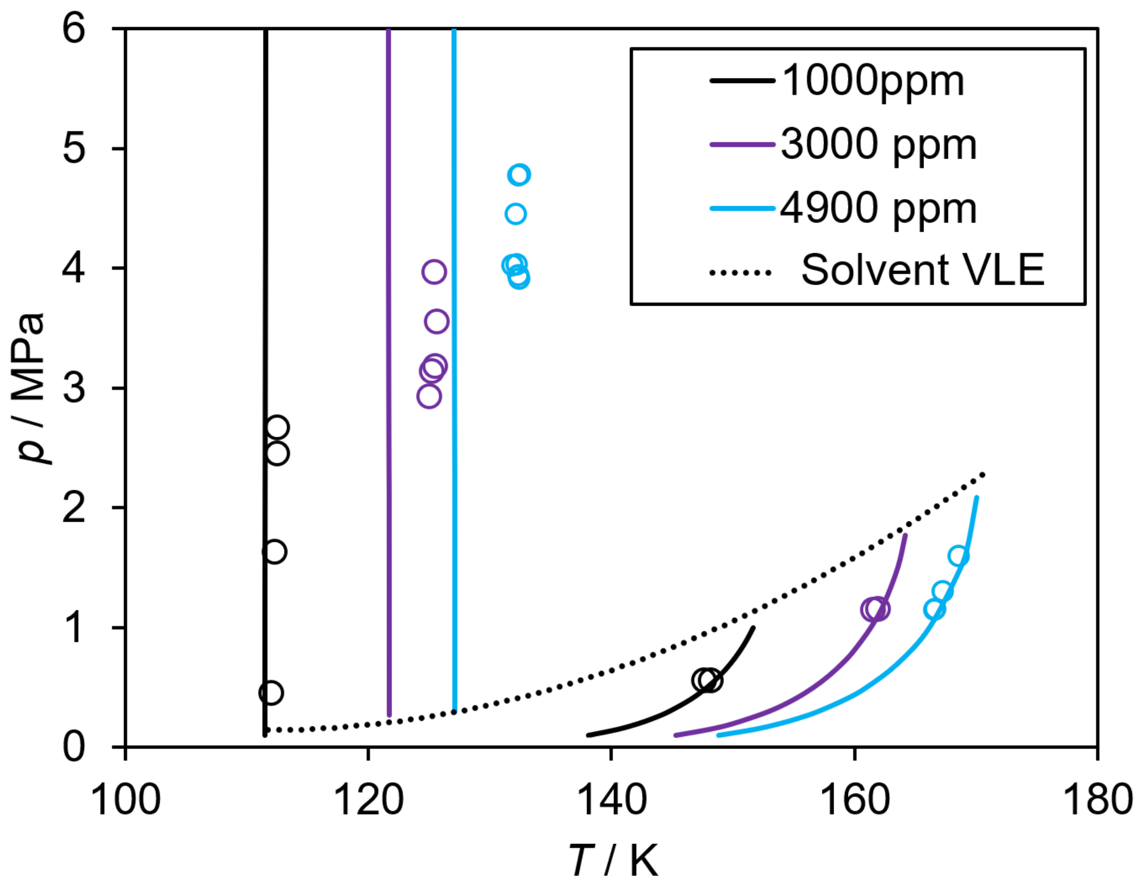



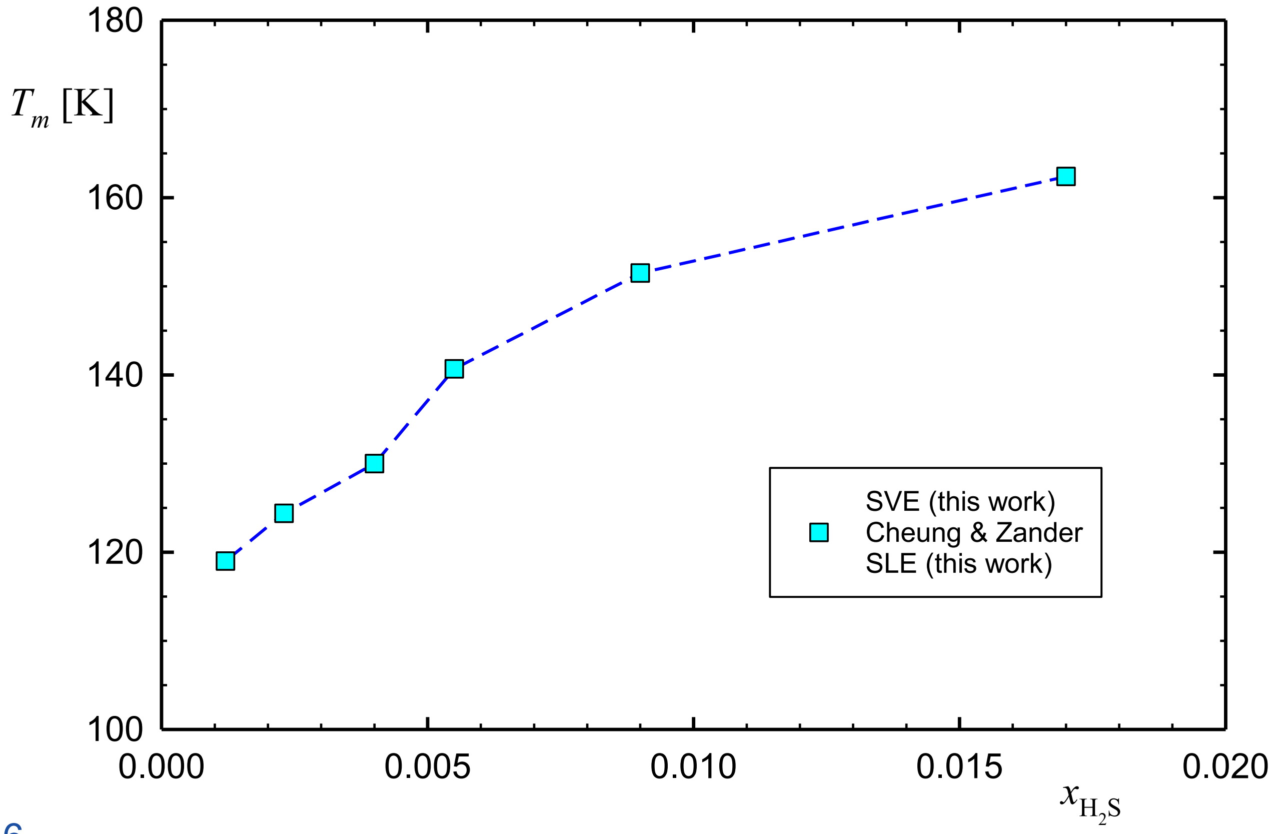
# Summary of Data: $H_2S$ in $CH_4$

New measurements compared with **untuned** models & literature data

Two datasets available:

- Cheung & Zander (1968), SLE, $T$ = (119-162) K; data relevant: $x_{H2S}$ = (1200 to 1700) ppm
- Kohn & Kurata (1958), SLLE & SLVE, $T$ > 167 K; data not relevant: (> 5.25 mol% $H_2S$)



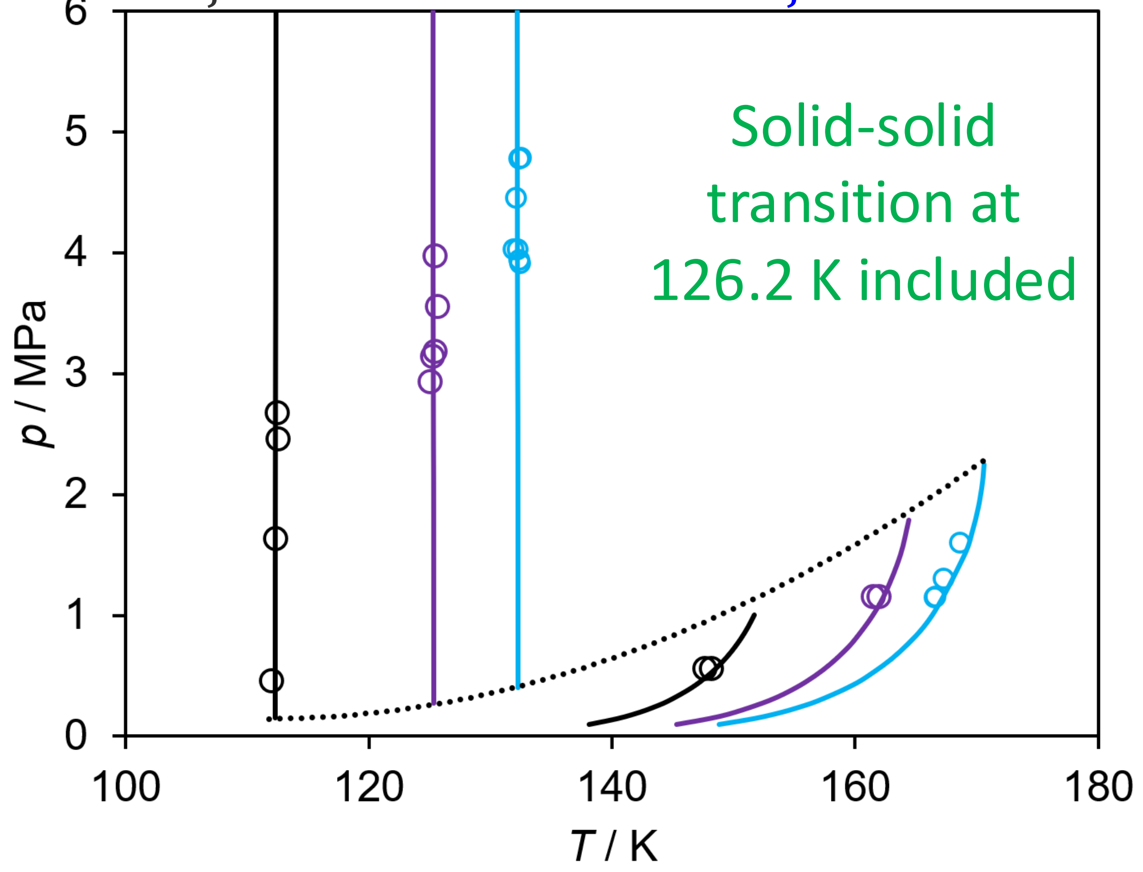



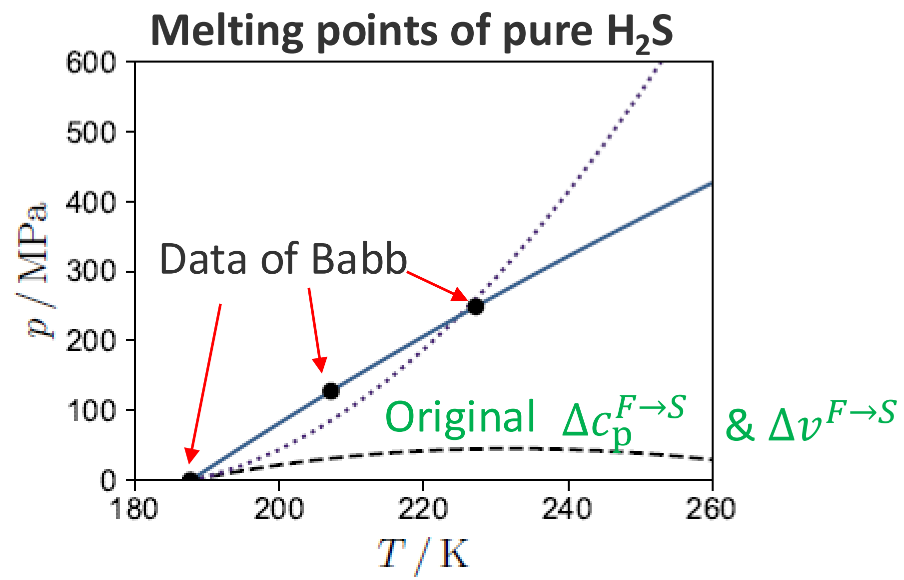
# Improved predictions: $H_2S$ in $CH_4$

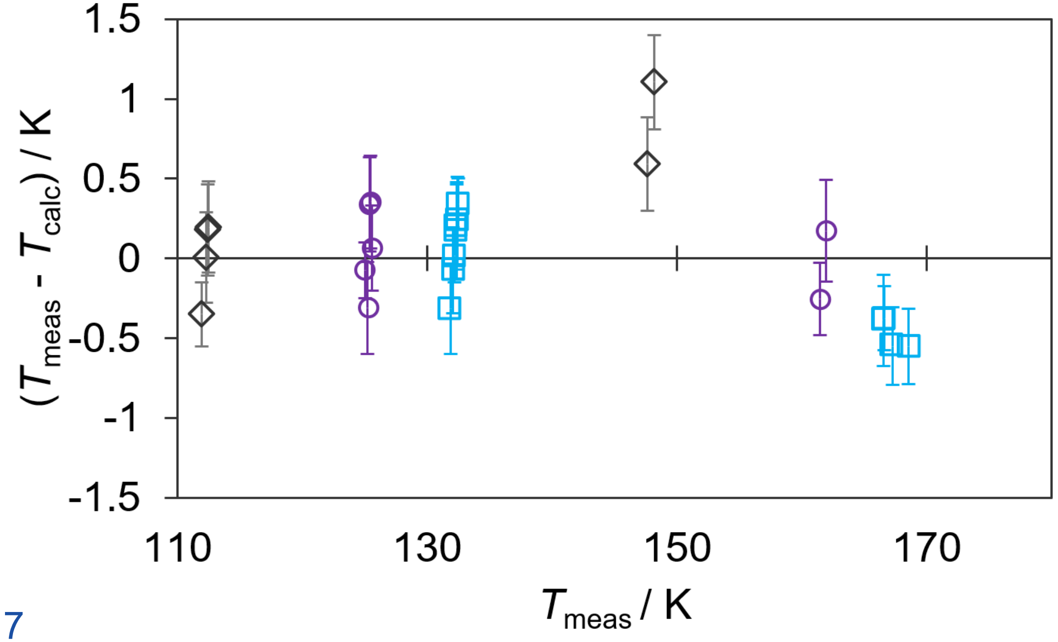
Data & model agreement improved by

- Tuning to pure $H_2S$ data: $\Delta c_p^{F\rightarrow S}$ $\Delta v^{F\rightarrow S}$
- Fitting PR EOS to solubility data:

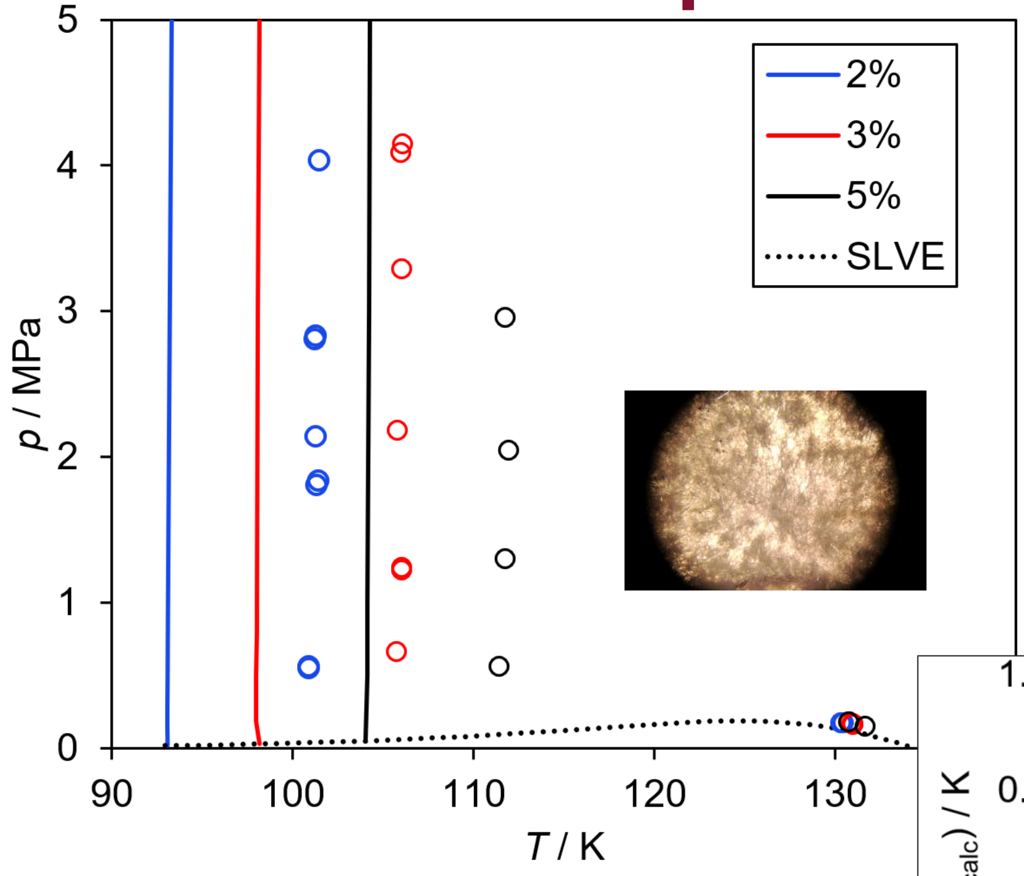
$k_{ij}^{(VLE)} = 0.081 \longrightarrow k_{ij}^{(SFE)} = 0.137$



# COS in $CH_4$

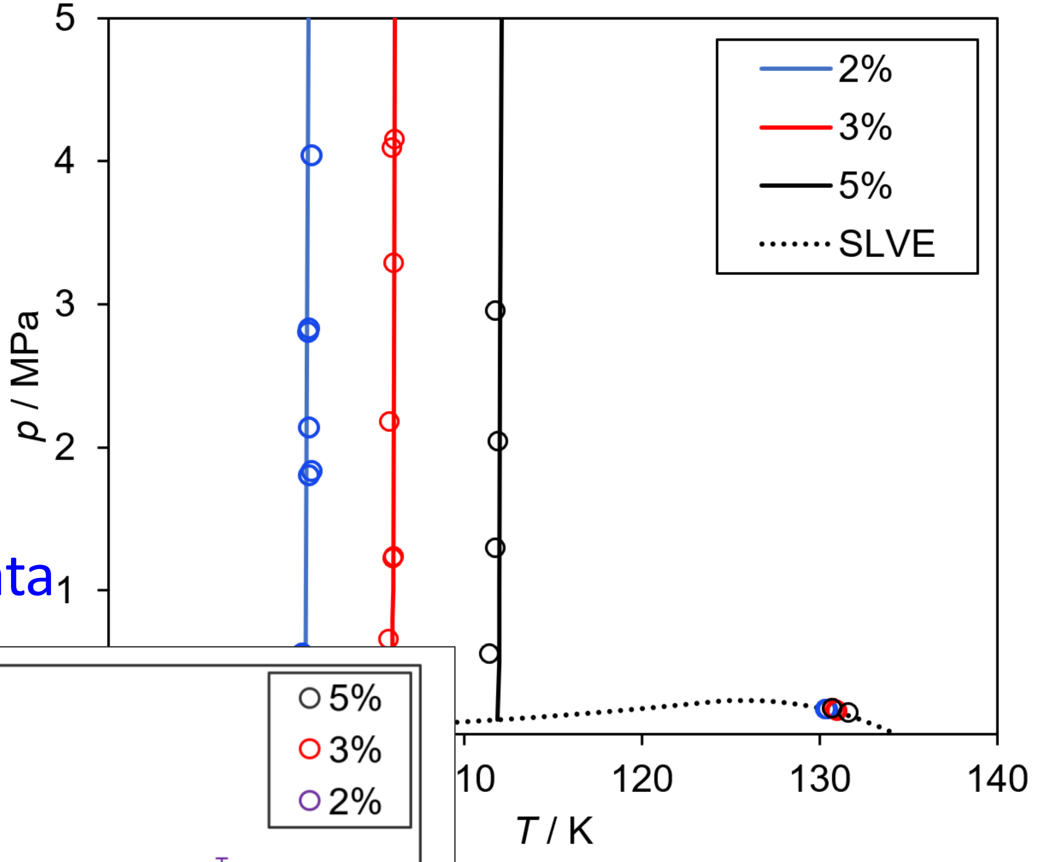


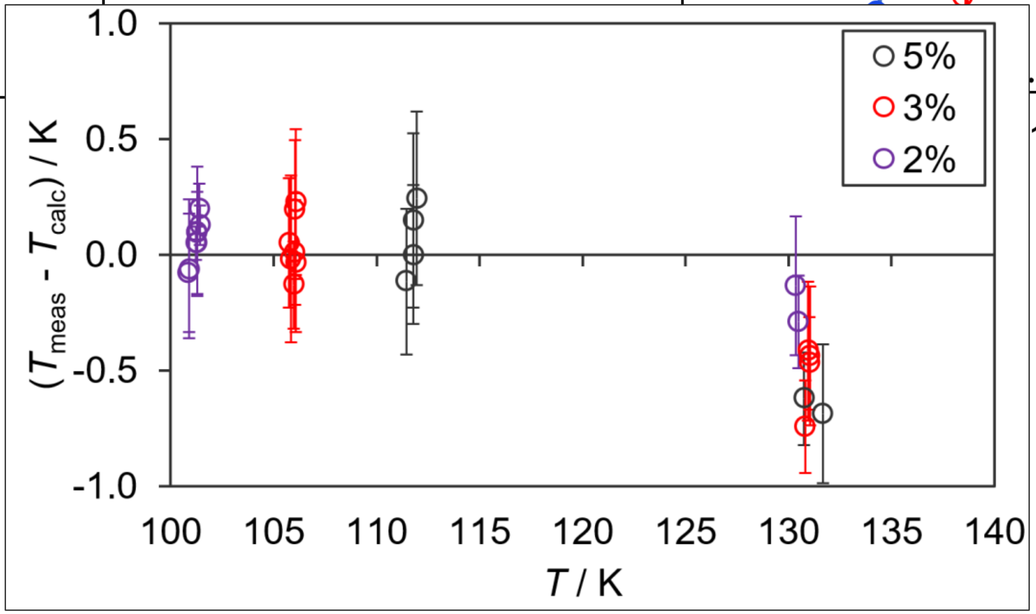

Fit to pure solid COS data

$\Delta c_p^{F \to S}$ $\Delta v^{F \to S}$

$k_{ij}^{(SFE)}$

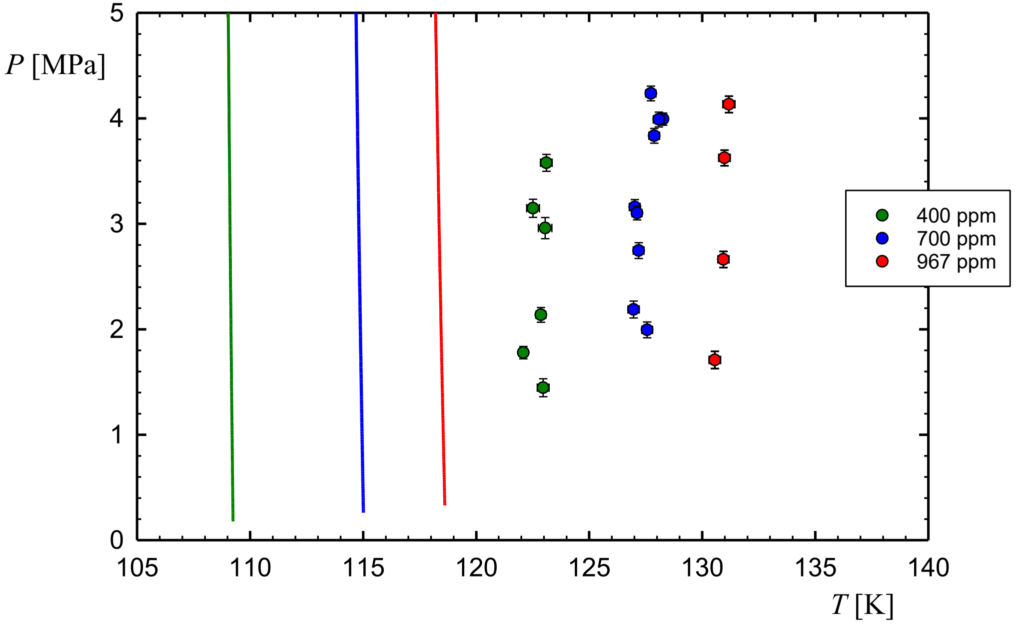
Fit to solubility data



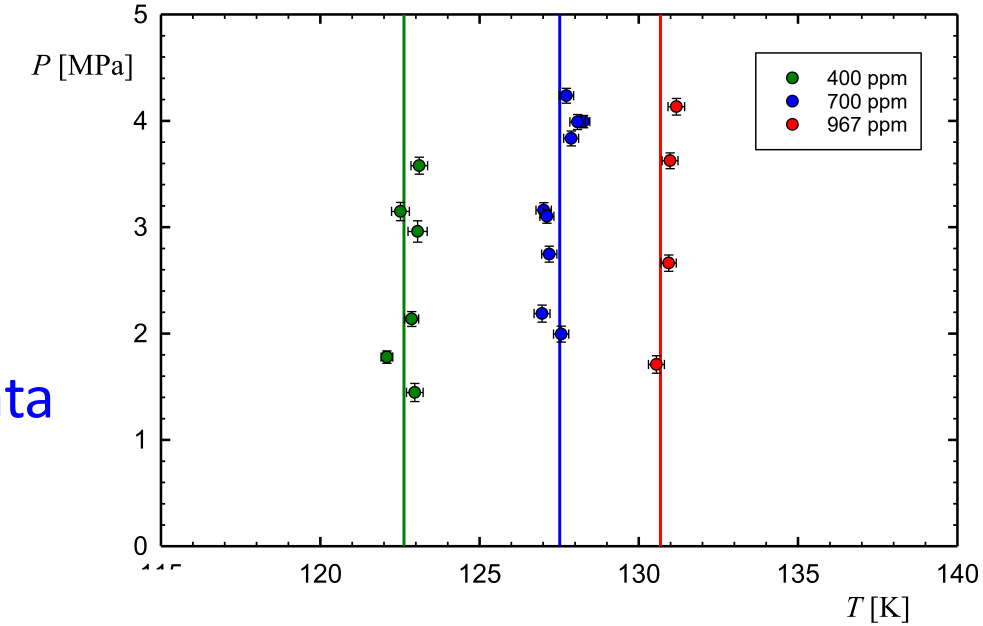

Hydrolysis of COS unlikely since no free $H_2O$: confirmed by sample analysis

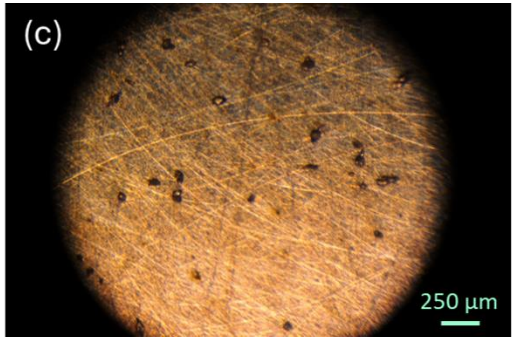
# Methanethiol (MeSH) in $CH_4$

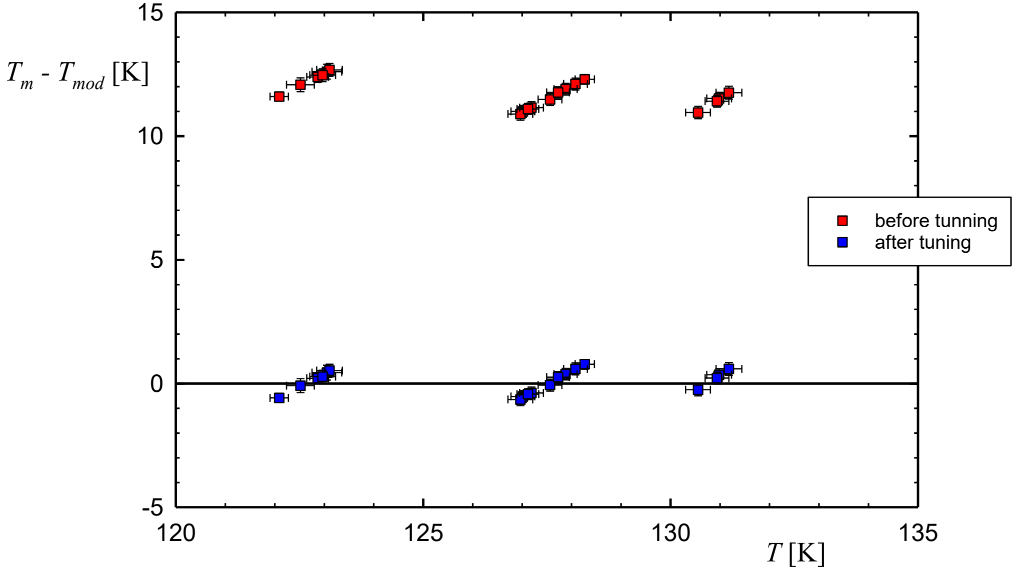



$k_{ij}^{(SFE)}$

Fit to solubility data

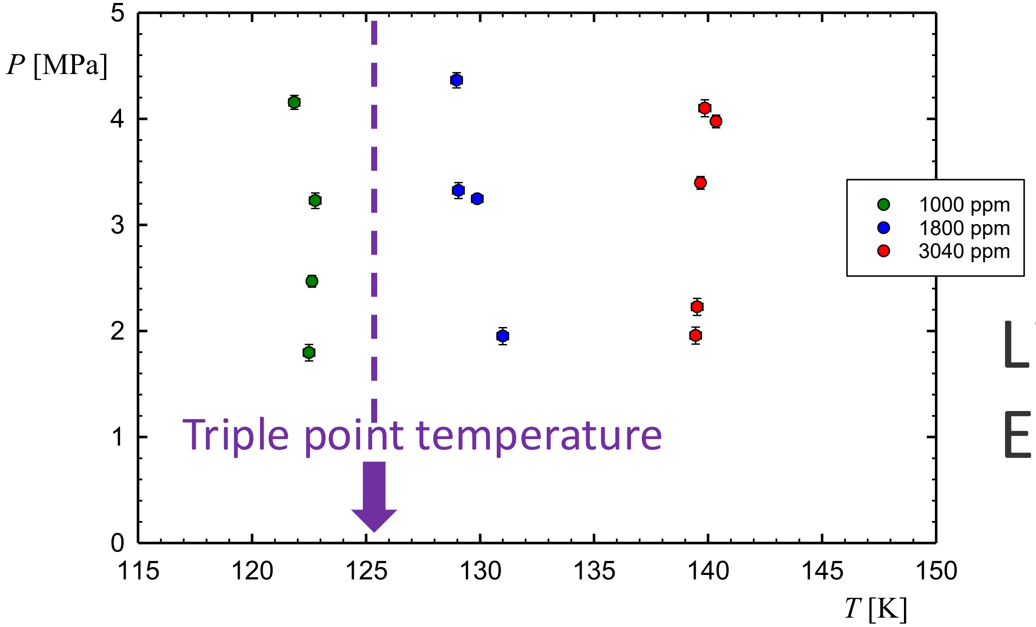


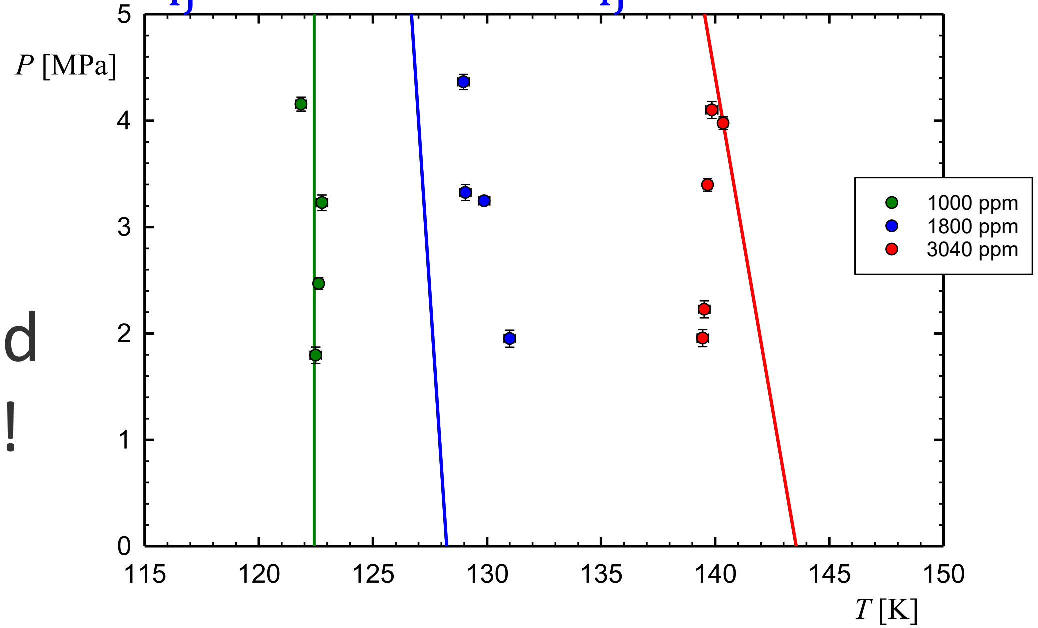

Solid-solid transition at 137.6 K included

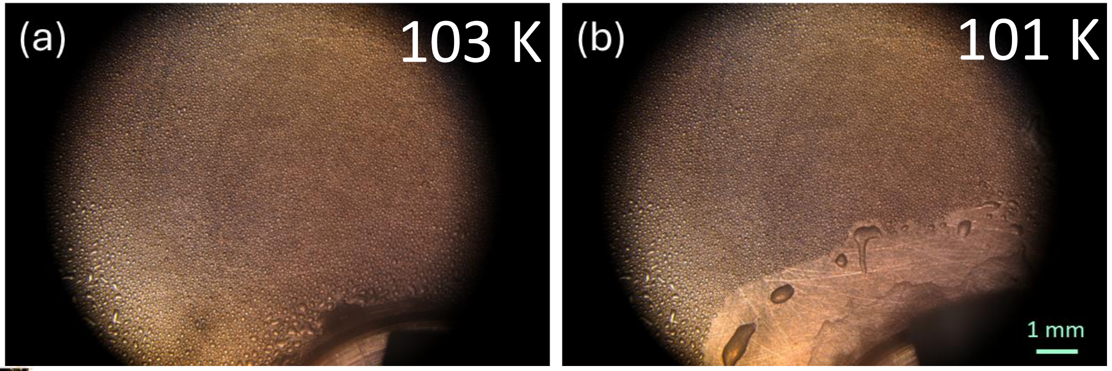
# Ethanethiol (EtSH) in $CH_4$

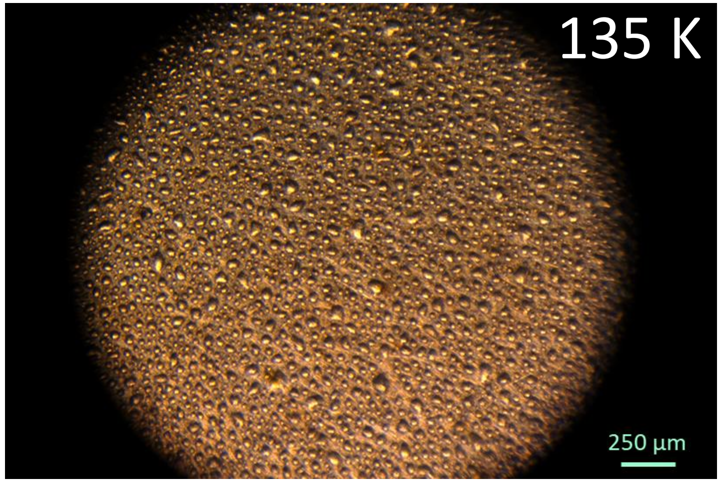



Liquid-Liquid Equilibrium!

$k_{ij}^{(SFE)} = 0.11 \quad k_{ij}^{(LLE)} = 0.102$



# New Approach:
# EOS for Solid $H_2S$

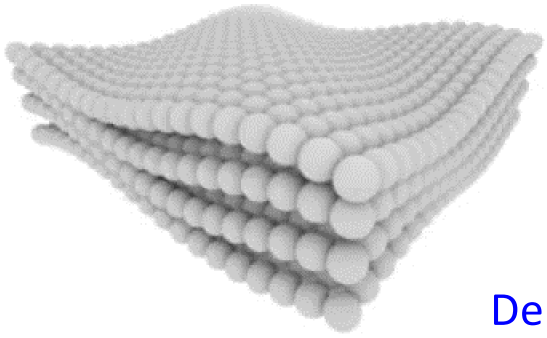
# Solid EOS can be more accurate

Classical method describes only 1 property of solid with just 3 parameters

→ Good if only limited thermodynamic data available for solid

Some solid impurities ($H_2O$, $CO_2$, Benzene, $H_2S$) are well-characterised over wide ($T$, $p$) range

→ Solid EOS fit to all thermodynamic property data should give more accurate predictions of its Gibbs Energy over ($T$, $p$) range



Use a physically-based model to describe energy stored in solid

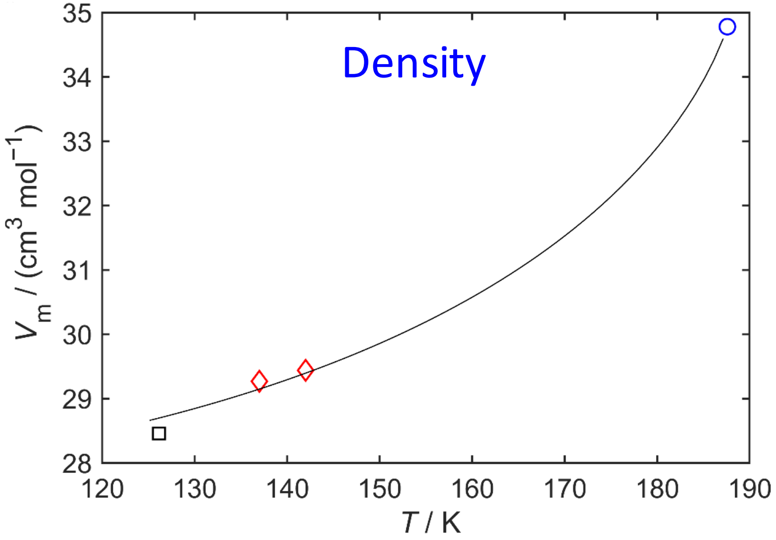
$$G_{solid}(T,p) = G_{lattice} + G_{internal} + G_{anharmonic}$$

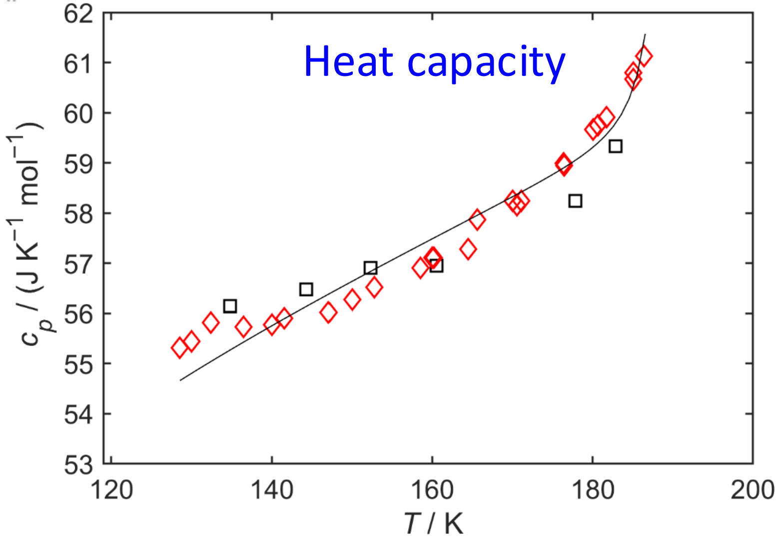
Density, heat capacity, phase boundary data    Spectroscopy    Deviations from ideal solid

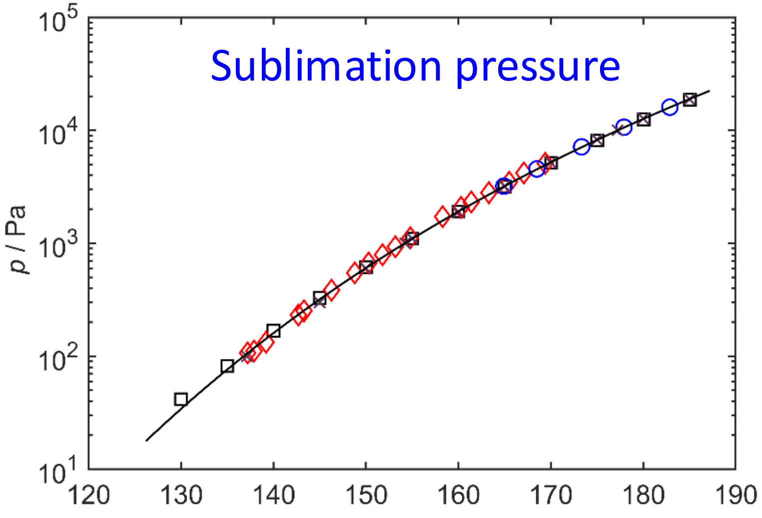
14 parameters fit to 82 data points for solid $H_2S$

# EOS for Solid $H_2S$ Phase I: Results

New EOS describes all data for solid $H_2S$ Phase I within their uncertainty from 126.2 K to triple point temperature (190.9 K)



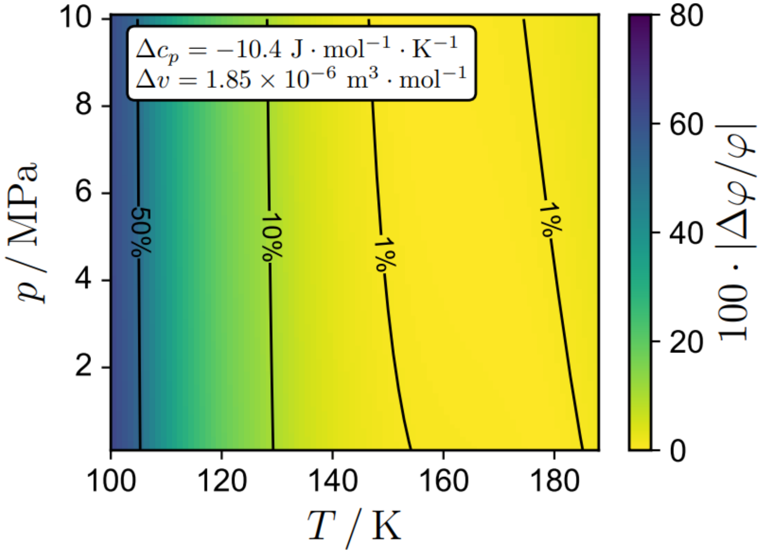




Helps confirm the best Classical method parameters

Other S-compounds have insufficient data

Working on getting better accuracy with few data



# Conclusions - Project 213

1. Models to predict solubility of 19 S-containing compounds in LNG built and implemented in free *ThermoFAST* software

https://thermofastweb.net

ThermoFAST Web
Online Thermodynamic Calculator

2. Sulphur-compatible apparatus to measure S-compound freeze-out in LNG demonstrated

3. Measured solubility of $H_2S$, COS, MeSH & EtSH in $CH_4$ at (100-140) K [-280 to -207 F] & pressures to 5 MPa [725 psia]

4. Tuned interaction parameters for these four binary mixtures to improve *ThermoFAST's* solubility predictions to within 0.5 K [0.9 F]

5. Developed new, accurate EOS for solid $H_2S$ phase I

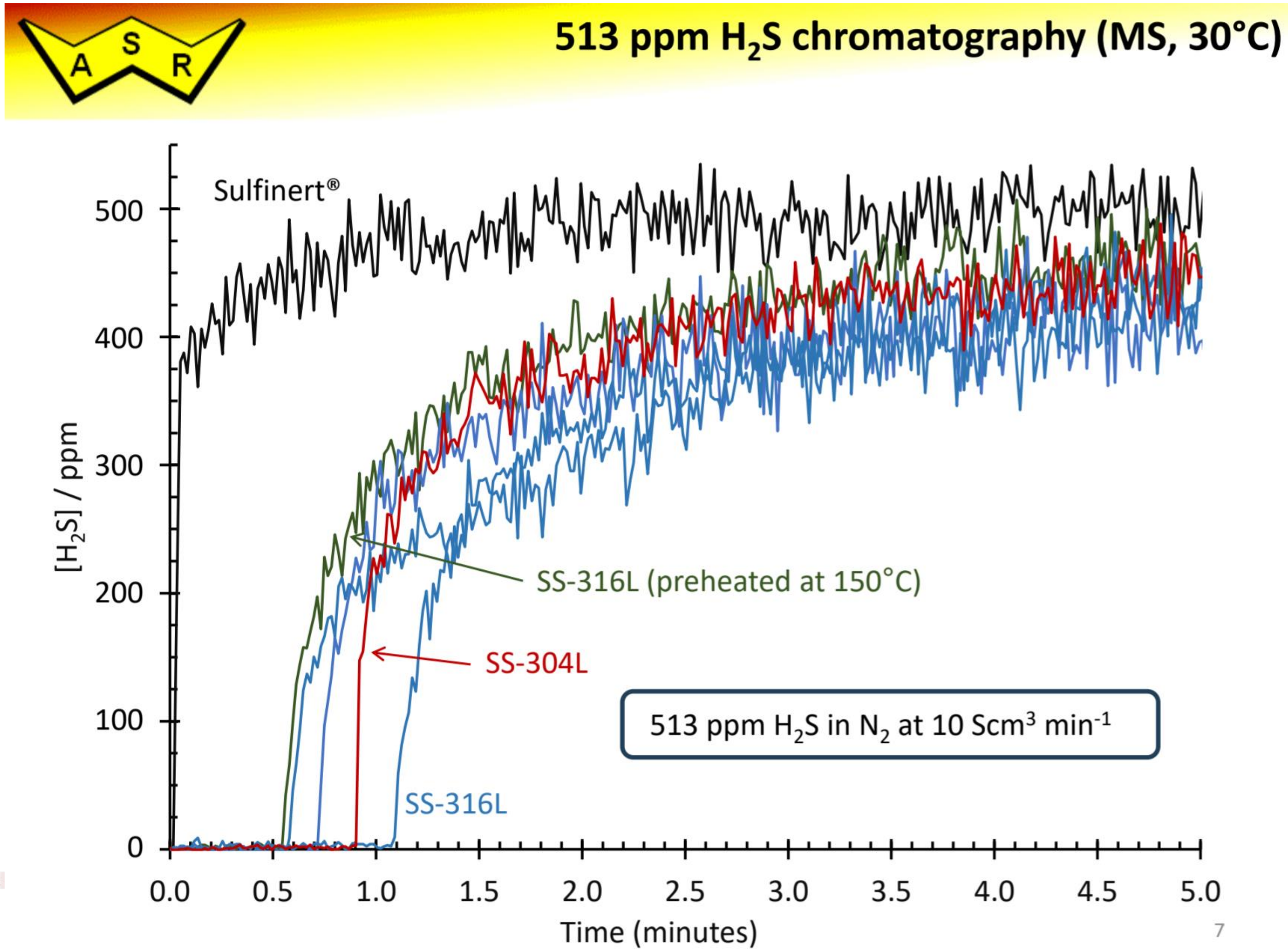
**2025-26: Extension to Project 213 with solubility of four new S-compounds in $CH_4$ to be measured**

FUTURE ENERGY EXPORTS
Cooperative Research Centre

# Thank you

# $H_2S$ Fade?

$H_2S$ has strong affinity for metal surfaces – *permanently* chemisorbs




UNIVERSITY OF CALGARY

$H_2S$ surface coverage on stainless steel ~ **180 µmol/m²**

CryoScope surface area
about 0.005 m²
*(inlet tubing, cell walls, cell base)*

**Amount of $H_2S$:**

- SLE: (140 to 630) µmol
- SVE: (2 to 10) µmol

# $H_2S$ Fade?

**Unmitigated $H_2S$ adsorption** could reduce the concentration of $H_2S$ in the measurement cell (wetted area 0.005 $m^2$, volume 5.3 $cm^3$)

| $x_{H2S}$ / ppm | Phase | $n_{H2S,ads}$ / µmol | $H_2S$ loss / ppm | Change in SFE $T$ / K |
|---|---|---|---|---|
| 4900 | SLE | 0.083 | -0.64 | 0.00 |
| 4900 | SVE | 0.083 | -42.2 | 0.08 |
| 3000 | SLE | 0.083 | -0.62 | 0.00 |
| 3000 | SVE | 0.083 | -39.6 | 0.12 |
| 1000 | SLE | 0.083 | -0.60 | 0.00 |
| 1000 | SVE | 0.083 | -36.4 | 0.27 |

Fortunately, **passivation** (by exposure to $H_2S$-containing mix) can mitigate future adsorption