# ÉTUDE DE LA DISSOLUTION DE L'HYDROGÈNE DANS LA SAUMURE DANS LE CADRE DU STOCKAGE EN NAPPE AQUIFÈRE

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**Chaire** junior **HYDR**

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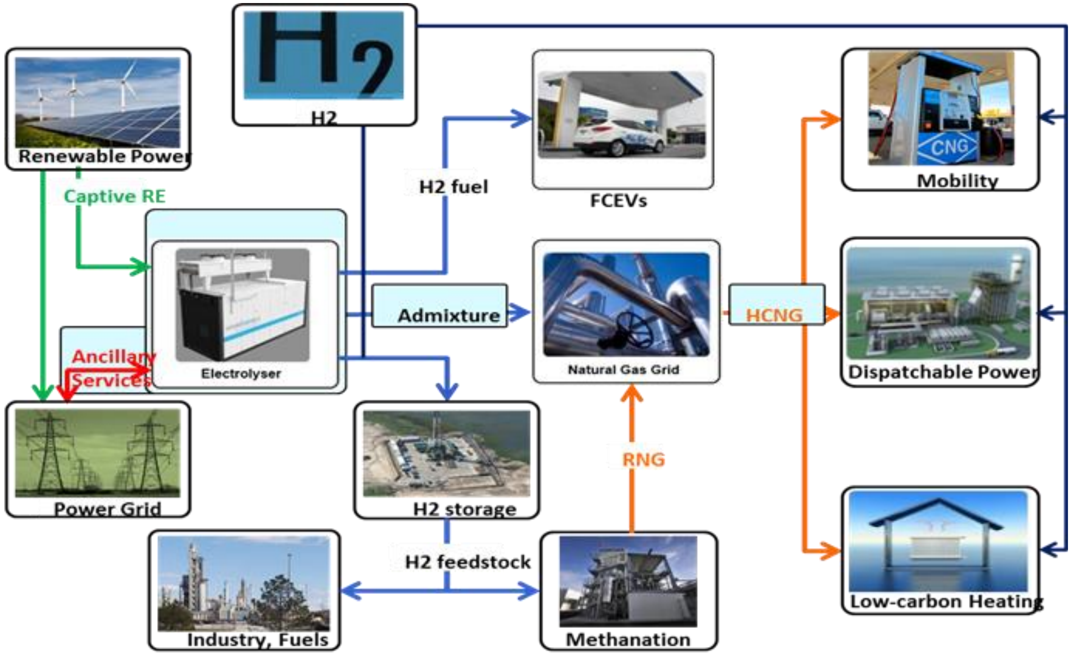
Durée : 5 ans

# RESEARCH PROJECT: JUNIOR CHAIR HYDR

## Scope

- ✓ **$H_2$ (+ NG and/or $CO_2$) mobility** in **Aquifers**
- ✓ **$H_2$** Storage**, Natural $H_2$** exploration**,** and **Geothermal** energy



## Framework (E2S)

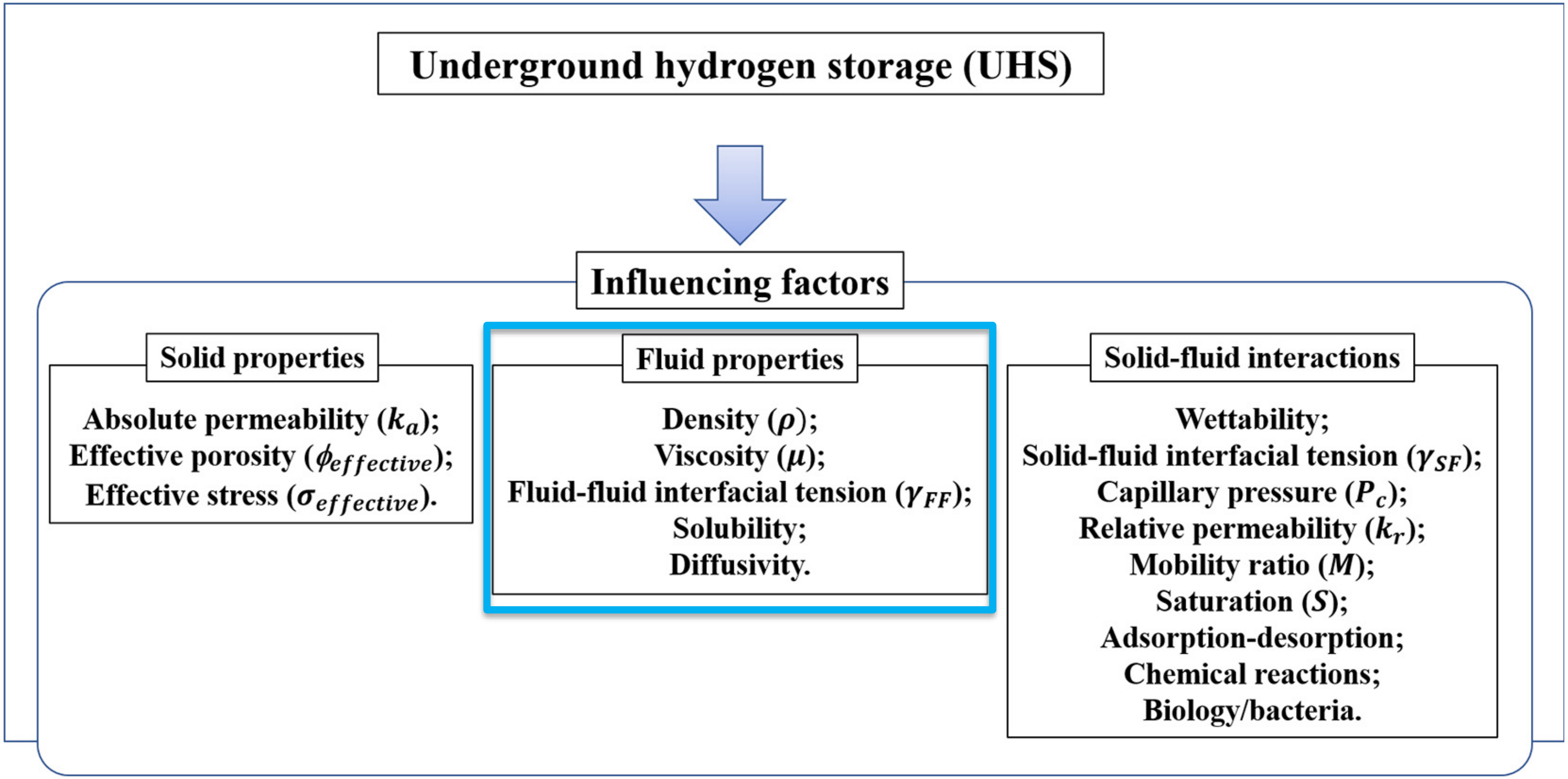
- ✓ **HYDR** Junior **Chair (S. Chabab)**
- ✓ **Exps + Mol Sim + EoS Models**
- ✓ **LFCR** + **LATEP** + **ProSim** + **IFPEN**

## Activities/Projects

- ○ **PhD (2021-2024, H. KERKACHE): Solubility + Diffusion** in **brine** and **clay. Mol Sim + exps**
- ○ **PDRA (2022-2024, ProSim): Advanced Modeling**
- ○ **Implementation** in ProSim Tools

# RESEARCH PROJECT: JUNIOR CHAIR HYDR

## Multi-scale parameters relevant in Underground Hydrogen Storage



**Underground hydrogen storage (UHS)**

**Influencing factors**

**Solid properties**

Absolute permeability ($k_a$);
Effective porosity ($\phi_{effective}$);
Effective stress ($\sigma_{effective}$).

**Fluid properties**

Density ($\rho$);
Viscosity ($\mu$);
Fluid-fluid interfacial tension ($\gamma_{FF}$);
Solubility;
Diffusivity.

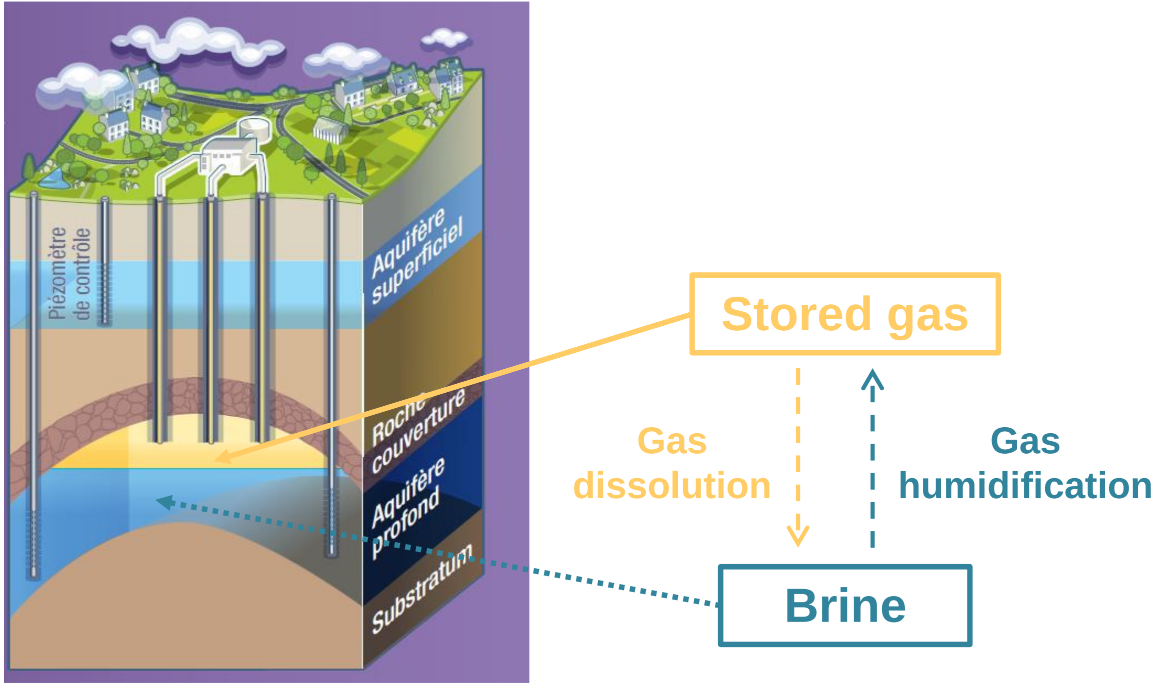
**Solid-fluid interactions**

Wettability;
Solid-fluid interfacial tension ($\gamma_{SF}$);
Capillary pressure ($P_c$);
Relative permeability ($k_r$);
Mobility ratio ($M$);
Saturation ($S$);
Adsorption-desorption;
Chemical reactions;
Biology/bacteria.

*Ref : Pan et al. (2021). Advances in Colloid and Interface Science.*

# RESEARCH PROJECT: JUNIOR CHAIR HYDR

## Deep aquifers



Stored gas

Gas dissolution

Gas humidification

Brine

Ref : INERIS

## Fluid properties

- ❖ **Gas solubility**
- ❖ Water content in gas phase
- ❖ Diffusion coefficient
- ❖ IFT (MS)

➔ Estimation of storage capacities and losses by dissolution

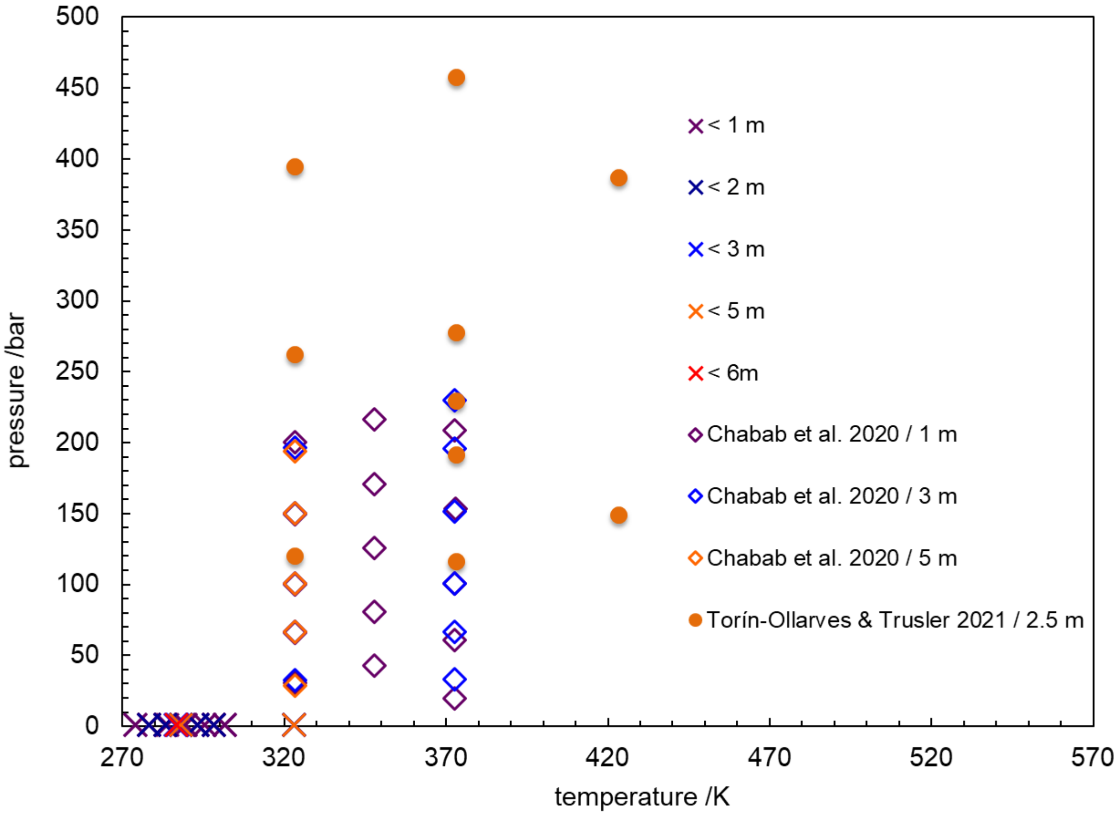
➔ Design / Simulation of surface facilities (e.g. gas dehydration after withdrawal)

➔ Gas reactivity study

➔ Estimate the amount of cushion gas

# REVIEW OF AVAILABLE $H_2$ SOLUBILITY DATA: INCONSISTENCIES

- Only 2 experimental studies ($P > P_{atm}$) :
  - Chabab et al. 2020 (**capillary sampling** + **GC** at known **T/P**)
  - Torín-Ollarves & Trusler 2021 (**bubble-point** pressure at known **T/x**)
- 1 MS study: Lopez-Lazaro et al. 2019



- Large deviations (up to **30%**) between the reported data

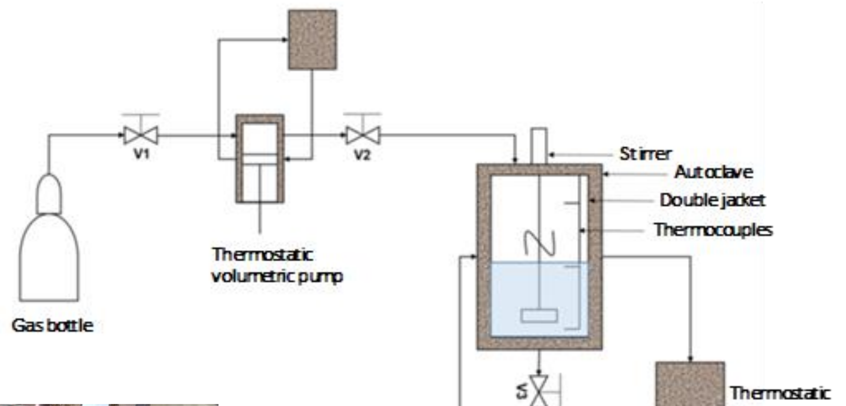
=> **Interest** to conduct **more studies: Experimental** and **Molecular Simulation !**

# **Apparatus** for measuring gas solubility in liquids: **presentation** and **validation** of the **protocol**

# CHARACTERIZATION OF $H_2$ (+ GAS) DISSOLUTION IN AQUIFERS

**Laboratory tests** (LaTEP lab)

Protocol development and validation



Phase equilibrium part

Potentiometric titration

Analysis part

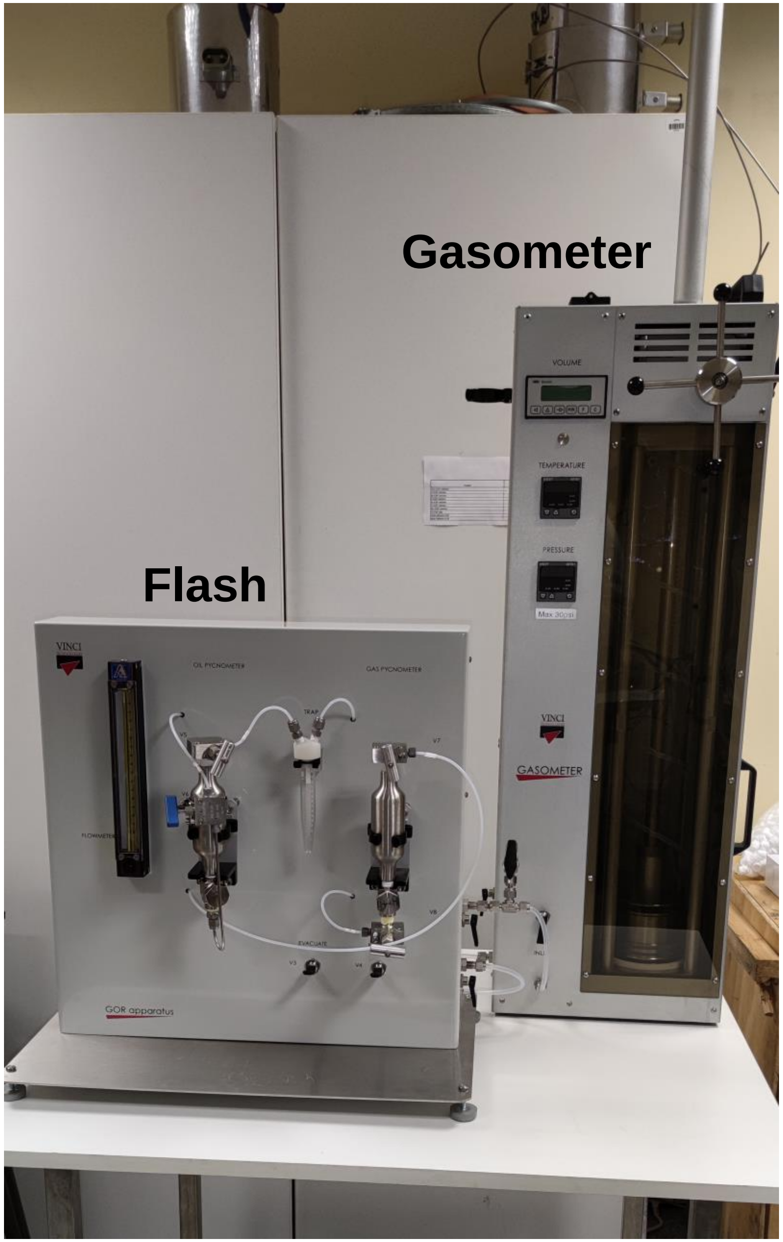
Sample collection in the Flash pycnometer

Adaptation of an existing apparatus

- Old analytical technique : potentiometric titration
- <u>New analytical technique</u> **: Volumetric** & **gravimetric**

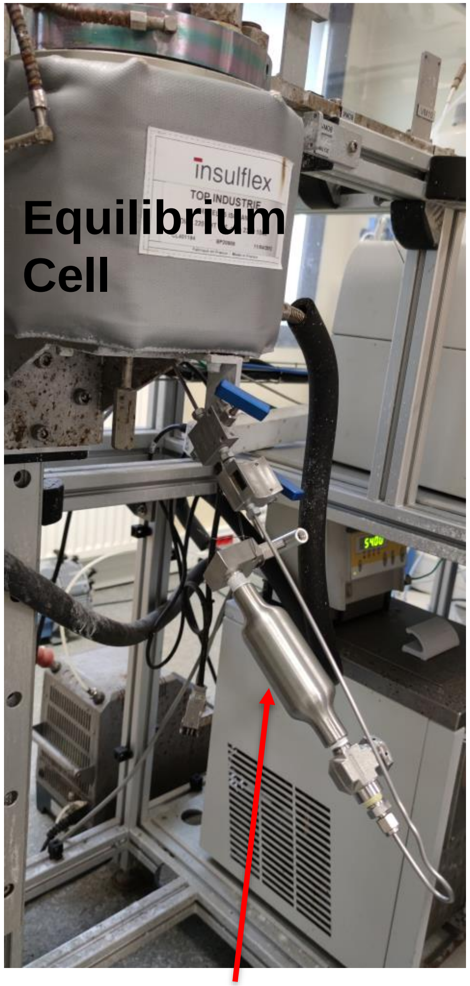
- Verification of pressure equipment
- Change of fluid : Change from a "Group 2 gas" fluid to a "**Group 1** gas" fluid

# CHARACTERIZATION OF $H_2$ (+ GAS) DISSOLUTION IN AQUIFERS


**Gasometer**

**Flash**

+ GC (if gas mixture)


**Equilibrium Cell**

**Sample collection in the Flash pycnometer**

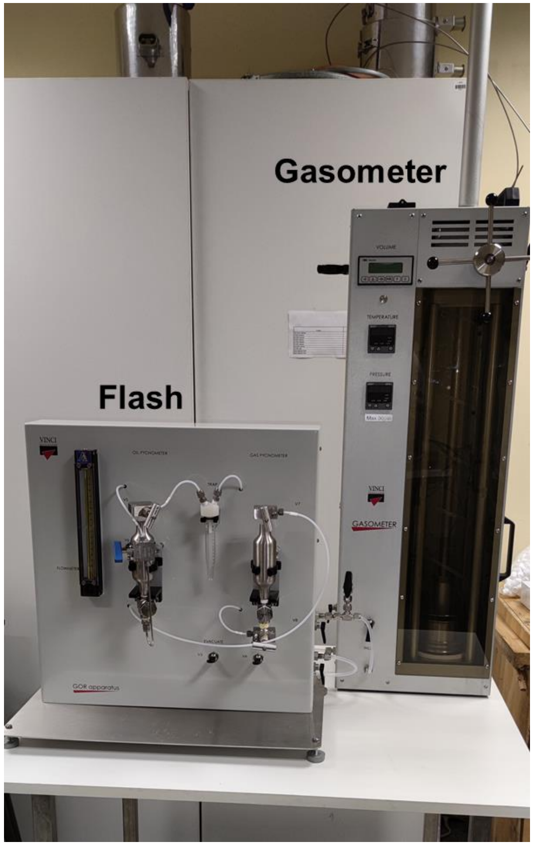
# CHARACTERIZATION OF $H_2$ (+ GAS) DISSOLUTION IN AQUIFERS

## Sampling and analysis

**$m_0$**

**Sampling**

**$m_1$**

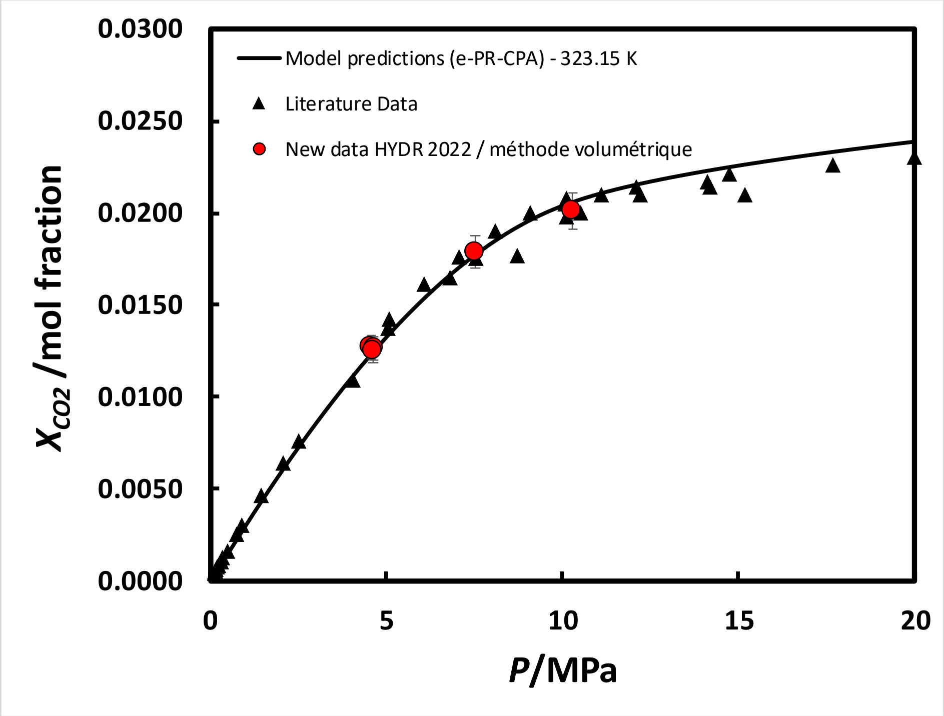


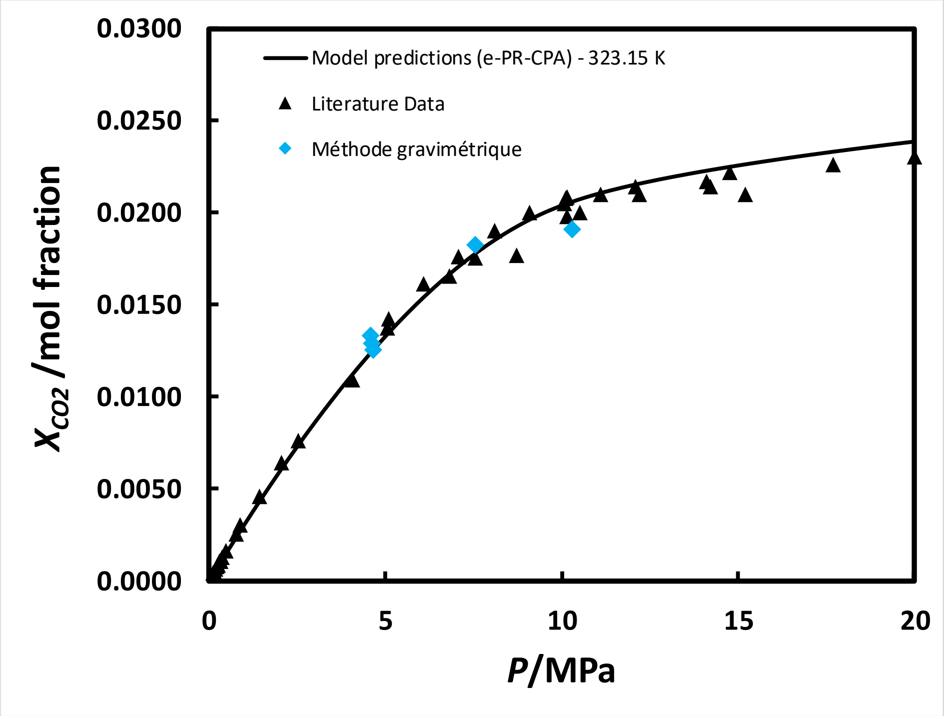
**Degassing**

**$m_2$**

# VALIDATION OF THE APPARATUS ON THE $CO_2$+$H_2O$ SYSTEM

## New data vs Literature data (for validation purpose)





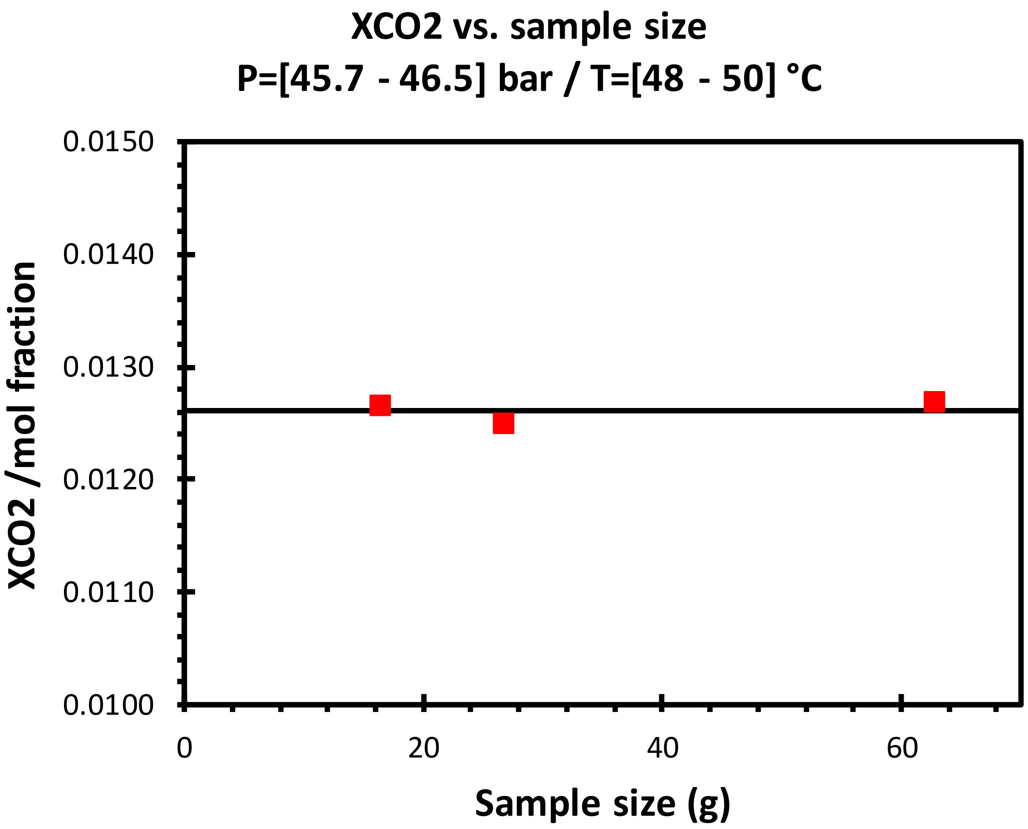
**Method 1 : Volumetric determination**

**Method 2 : Gravimetric determination**

| | P (MPa) | T ( K) | GLR (Nm3/m3) | Sample size (g) | $m_{Gas}$ (g) |
|---|---|---|---|---|---|
| **Pt1** | **4.57** | **321.55** | **15.81** | **62.85** | **1.96** |
| **Pt2** | **4.65** | **323.45** | **15.71** | **16.40** | **0.48** |
| **Pt3** | **4.63** | **323.45** | **15.65** | **26.82** | **0.81** |
| Pt4 | 7.53 | 323.15 | 22.95 | 36.15 | 1.58 |
| Pt5 | 10.30 | 324.75 | 26.13 | 10.47 | 0.48 |

Repeatability / reproducibility check

# CHARACTERIZATION OF $H_2$ (+ GAS) DISSOLUTION IN AQUIFERS



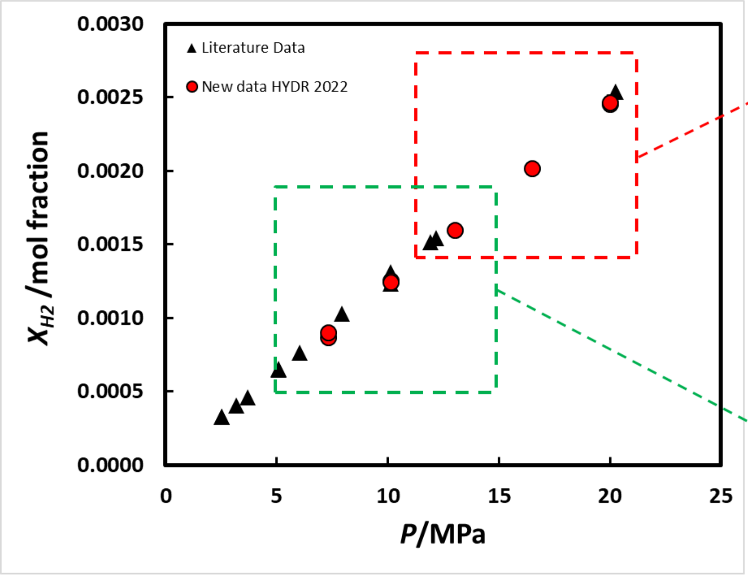
**Verification of the non-dependence on the sample size**

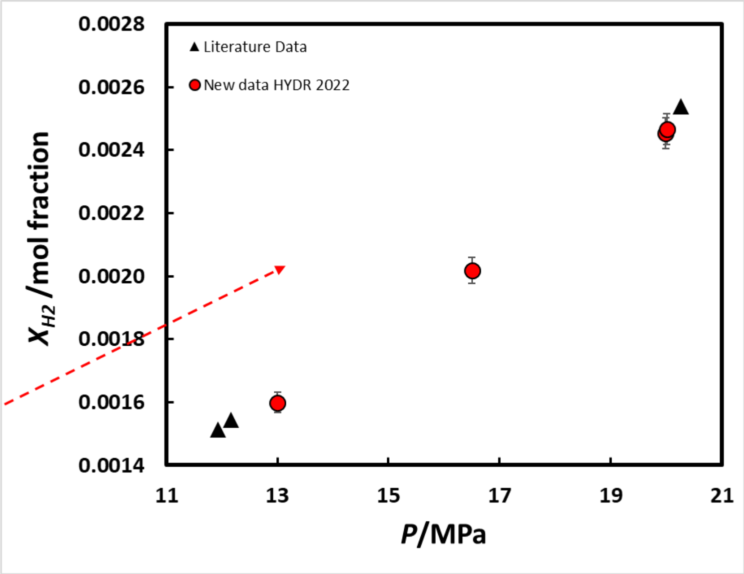
# Measuring the $H_2$ dissolution in water and brine

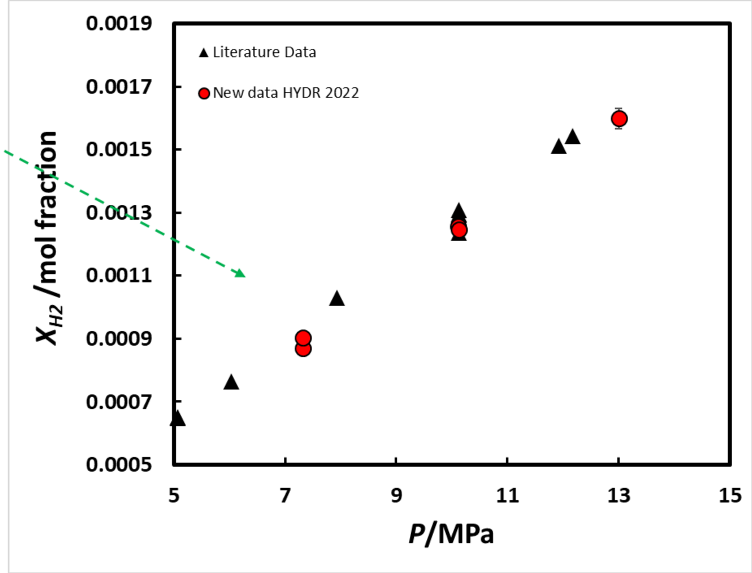
# CHARACTERIZATION OF $H_2$ (+ GAS) DISSOLUTION IN AQUIFERS

Measurements of **$H_2$** solubility in pure **$H_2O$**:

➔ 8 equilibrium points at 50° C (7 – 20 MPa)





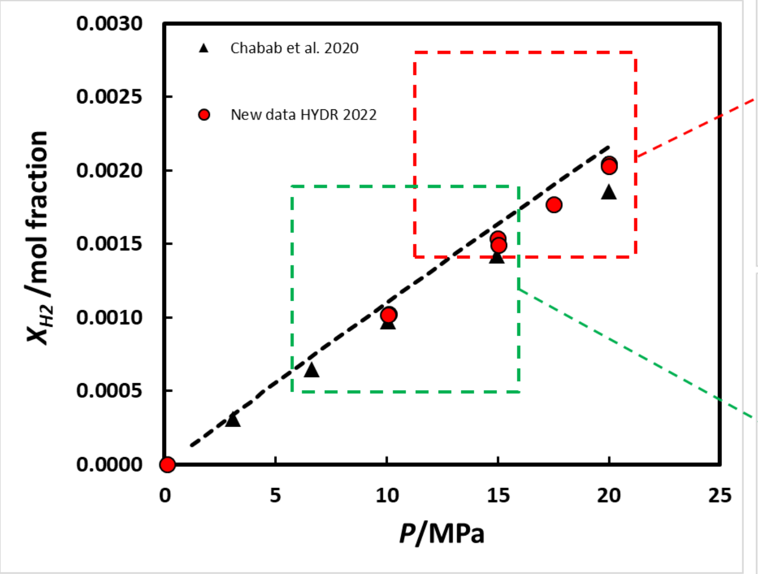


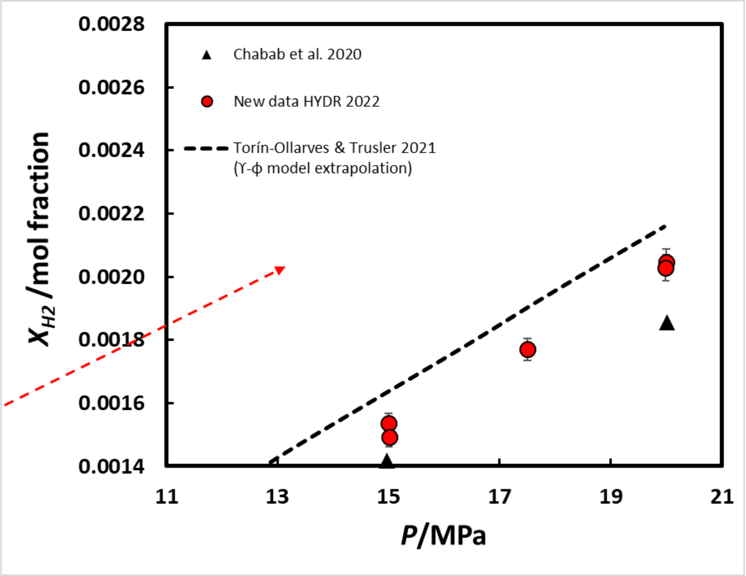
- ☐ Results **consistent** with literature data
- ☐ Due to the **low** $H_2$ **solubility**, measurements are **easier** at **high-pressure** (better repeatability and less uncertainty)

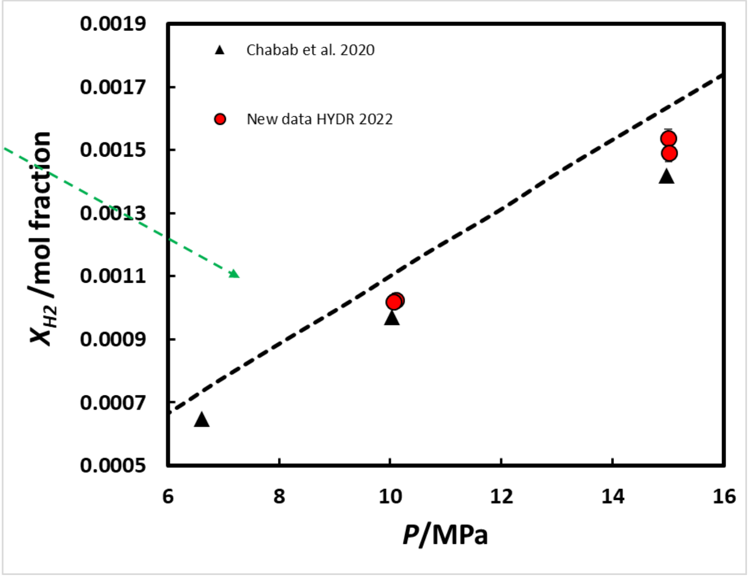
# CHARACTERIZATION OF $H_2$ (+ GAS) DISSOLUTION IN AQUIFERS

Measurements of **$H_2$** solubility in **1m NaCl** brine:

➔ 8 equilibrium points at 50° C (10 – 20 MPa)







- ☐ **Closer** to Torín-Ollarves & Trusler 2021 **than** Chabab et al. 2020 data
- ☐ Torín-Ollarves & Trusler 2021 and **this work** expect a **lower salting-out** than that reported by Chabab et al. 2020

# CHARACTERIZATION OF $H_2$ (+ GAS) DISSOLUTION IN AQUIFERS

Studying the **$H_2$** solubility using

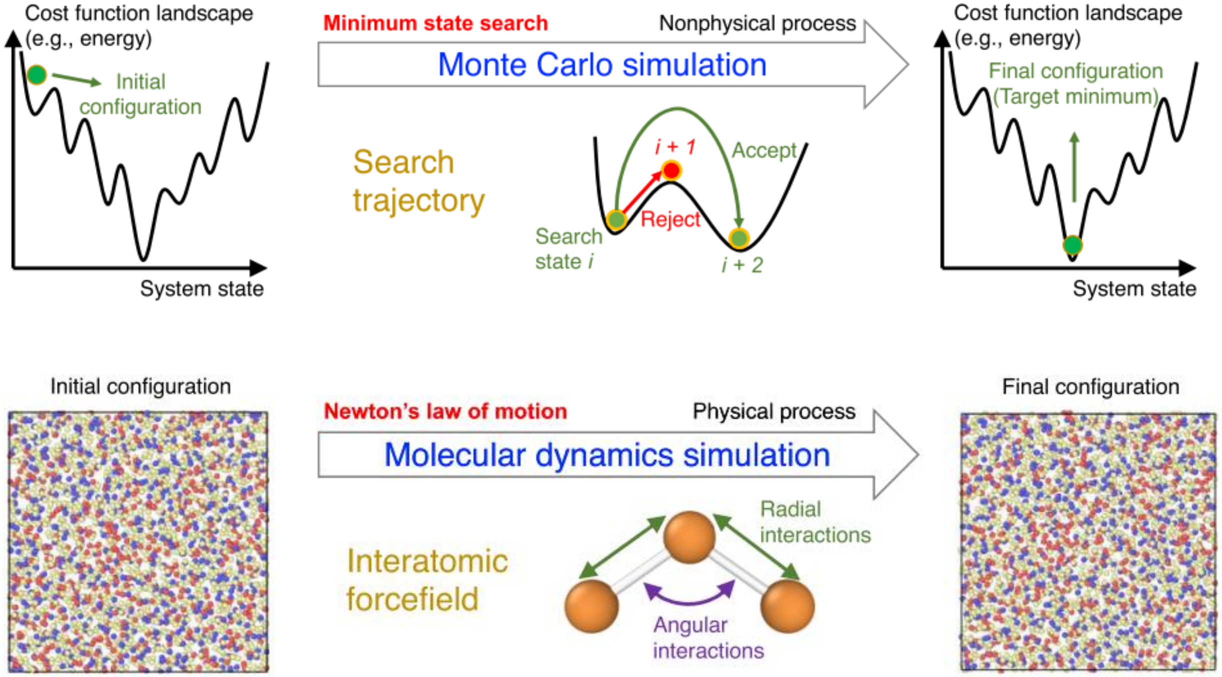
**Monte Carlo** simulation

# WHAT IS AND WHY MOLECULAR SIMULATION?

- High-performance computing (HPC)
- Force field
- Statistical method (Monte Carlo)
- Newton’s law of motion (Molecular Dynamics)

**Equilibrium properties** ( Density, Pression, Energy, ….)

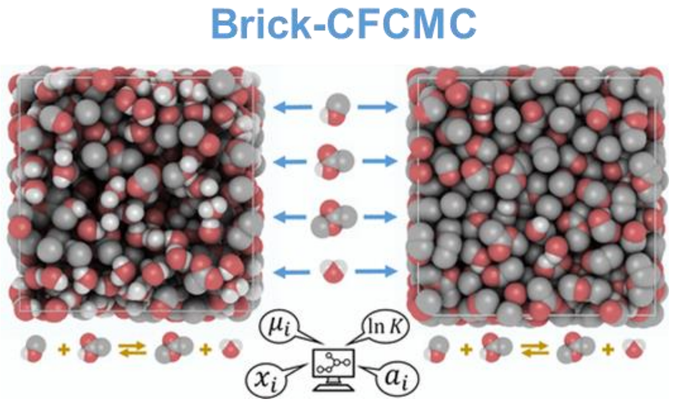
**Transport properties** (viscosity, diffusion coefficient, thermal conductivity)



Ref: Lachet, Véronique. "La simulation moléculaire: un outil au service de l’industrie." *l’actualité chimique* 340 (2010): 22.

# MOLECULAR SIMULATIONS: TOOLS AND MODELS

- 2 tools are used for the calculation of $H_2$ solubility by performing Monte Carlo simulations : **Towhee** and **Brick-CFCMC**



- Model choice :

**Pure $H_2$ model:** Alavi, Marx

**Pure $H_2O$ model:** SPC/E, TIP4P/2005

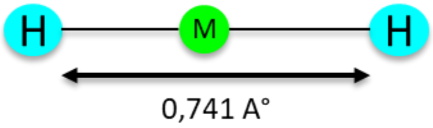
**Binary mixture :** Alavi_SPC/E - Alavi2005_TIP4P/2005 - Marx_TIP4P/2005 + Lorentez-Berthelot for mixing rule.

- Use of different methods for the calculation of solubility

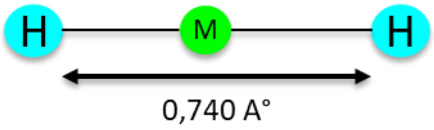
# MOLECULAR SIMULATIONS: FORCE FIELDS

## $H_2$

**Alavi 2005**

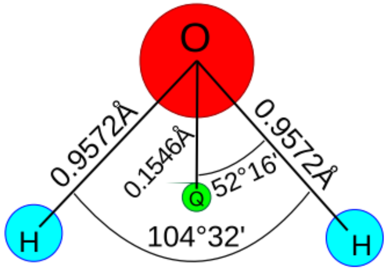


**Marx 1992**

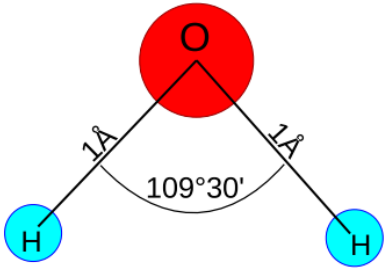


| Model/atom | q+ (e) | q- (e) | ε (K) | σ (A°) |
|---|---|---|---|---|
| **Alavi 2005** | | | | |
| H-$H_2$ | 0,4932 | - | - | - |
| M-$H_2$ | - | −0,9864 | 34,3 | 3,038 |
| **Marx 1992** | | | | |
| H-$H_2$ | 0,4680 | - | - | - |
| M-$H_2$ | - | −0,9360 | 36,7 | 2,958 |

## $H_2O$



TIP4P/2005

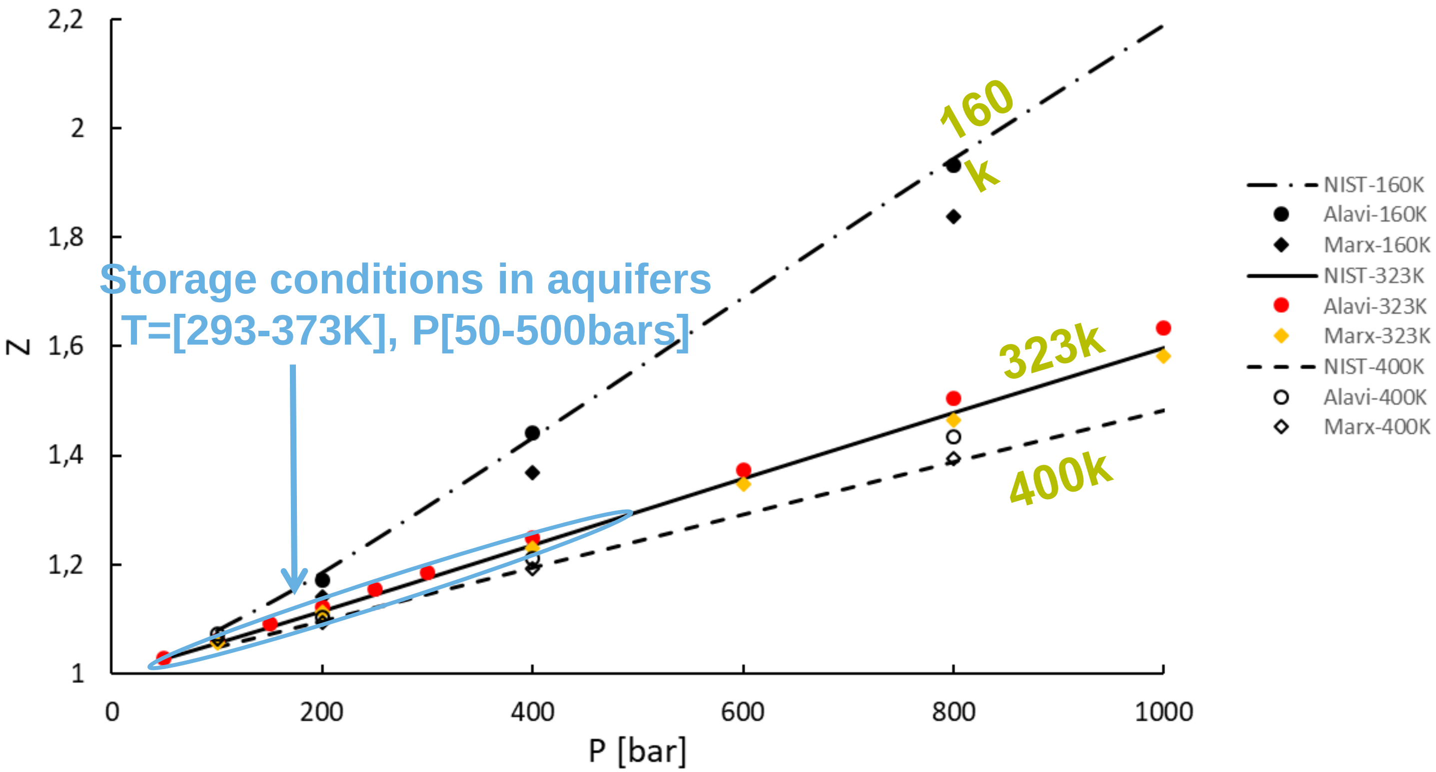


SPC/E

Ref: Vinš, Václav, et al. "Molecular simulations of the vapor–liquid phase interfaces of pure water modeled with the SPC/E and the TIP4P/2005 molecular models."

| Model/atom | q+ (e) | q- (e) | ε (K) | σ (A°) |
|---|---|---|---|---|
| **SPC/E** | | | | |
| O | - | −0,8476 | 78,175 | 3,166 |
| H | 0,4932 | - | - | - |
| **TIP4P/2005** | | | | |
| O | - | - | 93,196 | 3,1589 |
| H | 0,5564 | - | - | - |
| Q | - | −1,1128 | - | - |

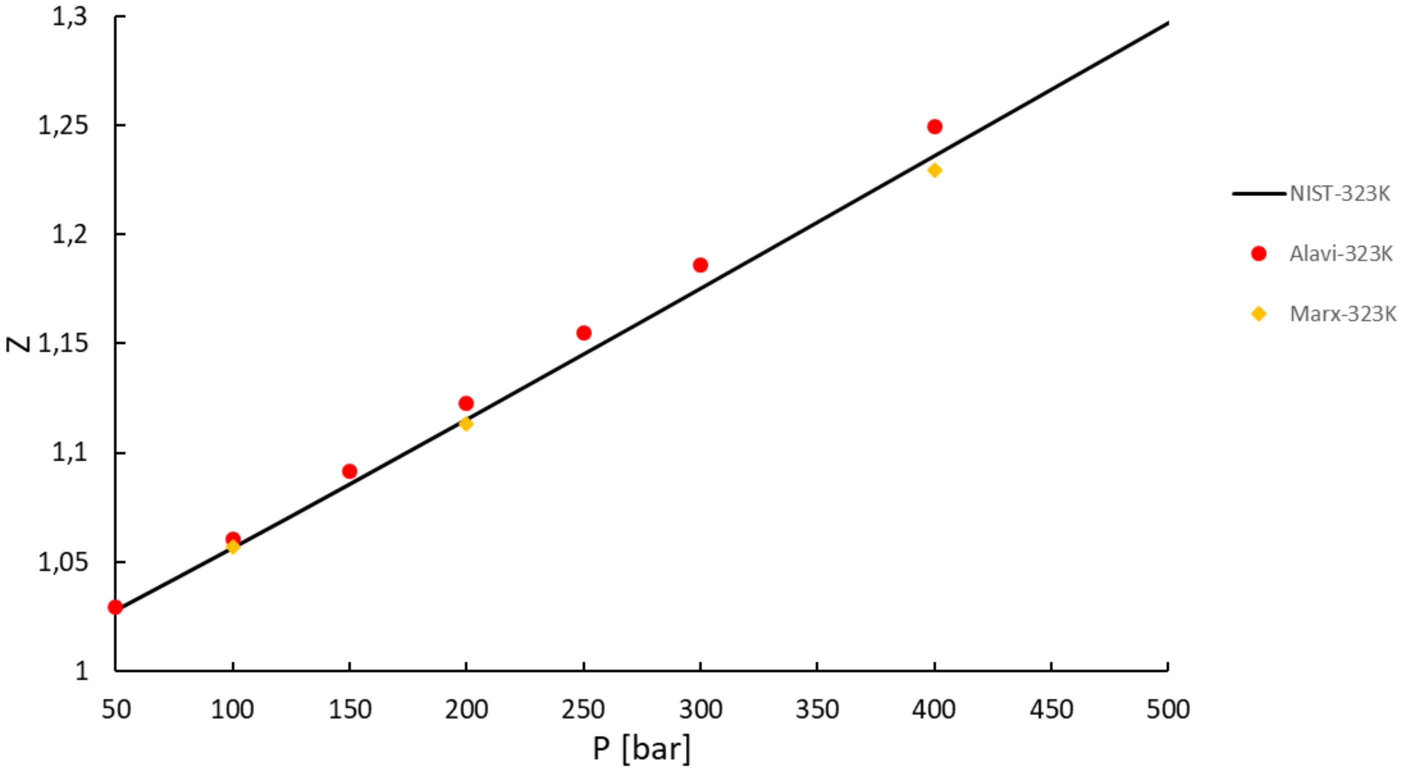
# EVALUATION OF FORCE FIELDS : PURE HYDROGEN $H_2$



- **<u>At 160K:</u>** Among the two models tested, the Alavi model captures well the compressibility factor ($AAD_{Alavi}$=1,5%) at low temperature and so the quantum effects.

- **<u>At 400K</u>**: The model of Marx predict well the compressibility factor ($AAD_{Marx}$=0,49%), However, Alavi is less accurate at high temperature($AAD_{Alavi}$=2,17%).

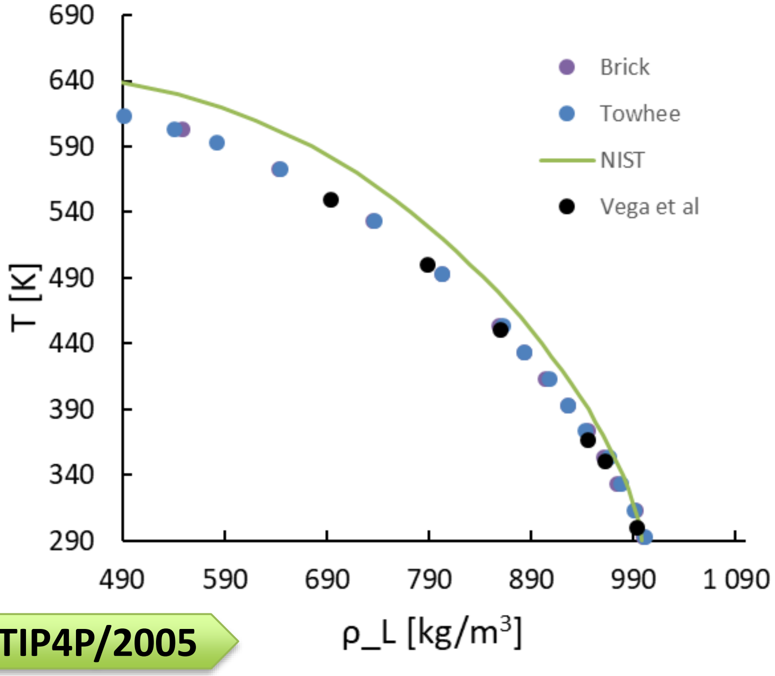
# EVALUATION OF FORCE FIELDS : PURE HYDROGEN $H_2$ AT 323 K

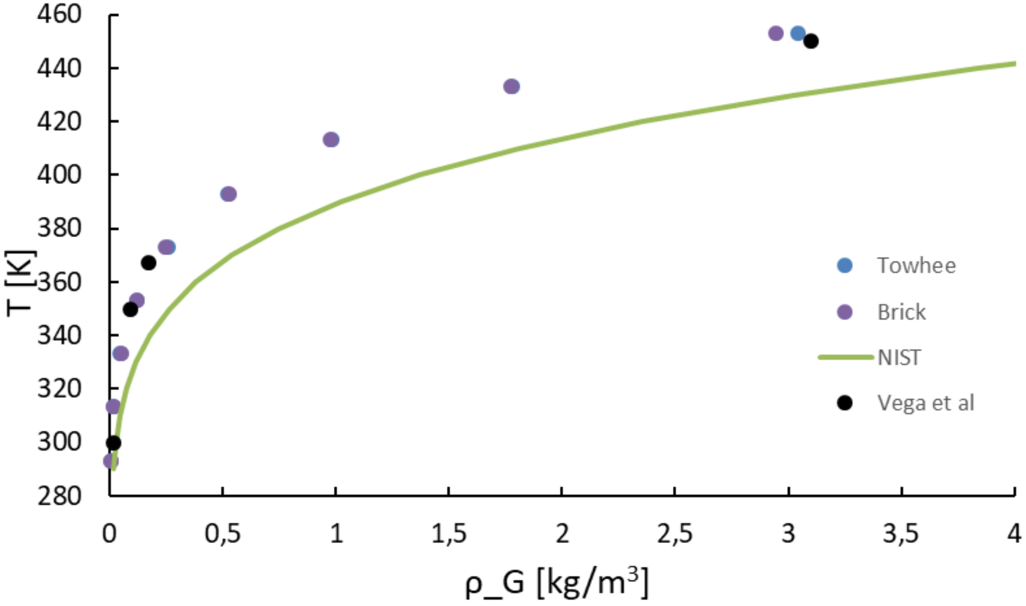


- **<u>At 323K: </u>** all the models predict well the compressibility factor, the AAD obtained are less than 1.($AAD_{Alavi}$=0,97%, $AAD_{Marx}$=0,53%)

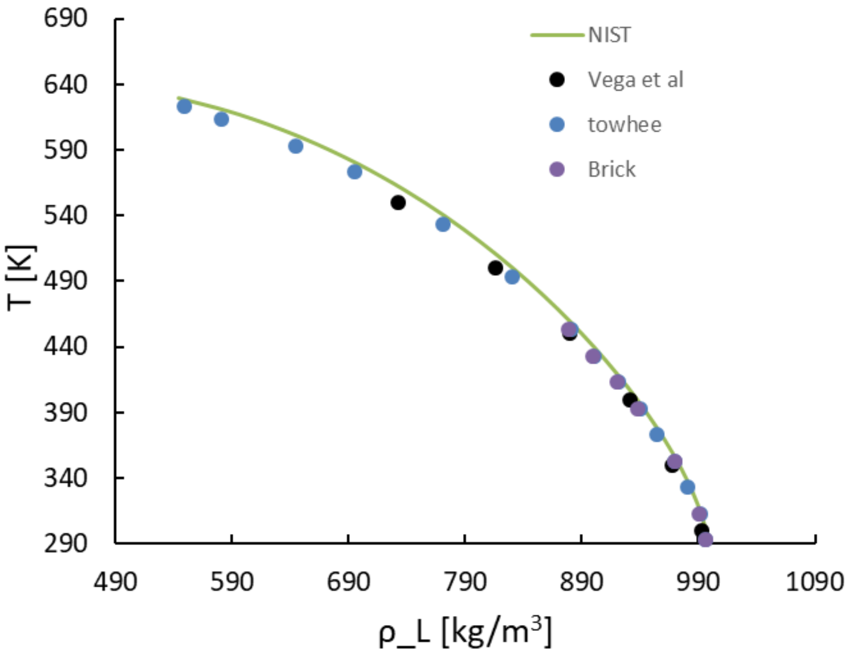
# EVALUATION OF FORCE FIELDS : PURE WATER $H_2O$

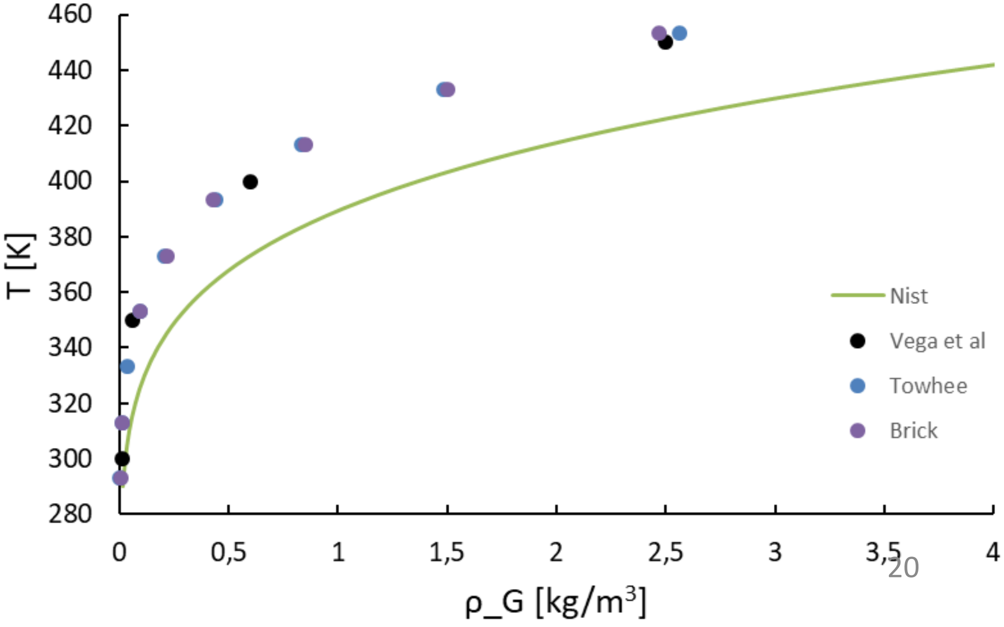
**SPC/E**





**TIP4P/2005**





# THE DIFFERENT METHODS FOR THE CALCULATION OF SOLUBILITY

- **$H_i$** : The solubility of hydrogen in water/brine can be calculated using the Henry constant, which is related to the residual chemical potential of the solute i at infinite dilution μi∞ :

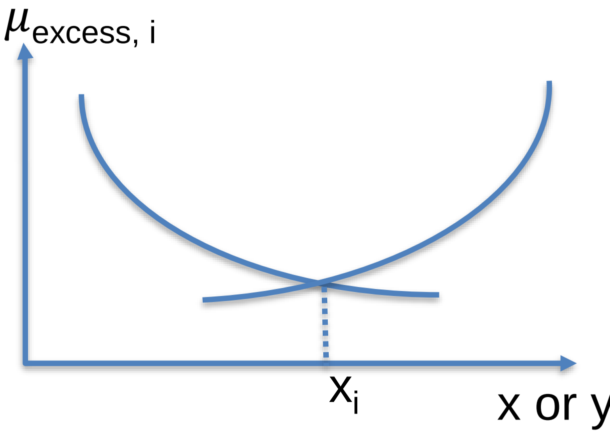
$$H_i = \rho k_B T \exp(\mu_i^\infty / k_B T)$$

where $k_B$ is the Boltzmann constant, T the temperature, ρ the density of the solvent.

$\mu_i^\infty$ : from molecular simulation (MSMC: 1 boxe-NPT ensemble + widom insertion)

- **using Gibbs ensemble** (2boxes -NPT ensemble)
- **Equality of chemical potentials:** NPT simulations => plot the chemical potential as a function of hydrogen composition => the intersection of the two curves (liquid and vapor) represents the solubility of hydrogen at the fixed conditions

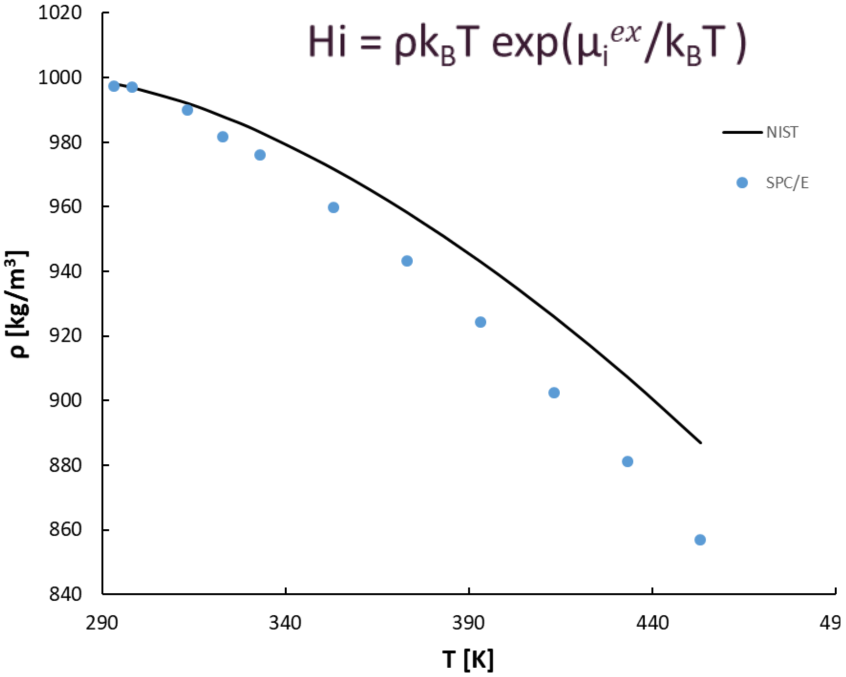
| | Vapor phase ($H_2$+$H_2O$) NPT ensembles | | Liquid phase ($H_2$+$H_2O$) NPT ensembles | |
|---|---|---|---|---|
| **N simulations** | **$H_2$** | **$H_2O$** | **$H_2O$** | **$H_2$** |
| 1 | 600 | 1 | 730 | 1 |
| 2 | 600 | 2 | 730 | 2 |
| 3 | 600 | … | 730 | … |
| 4 | 600 | … | 730 | … |
| … | … | … | … | … |

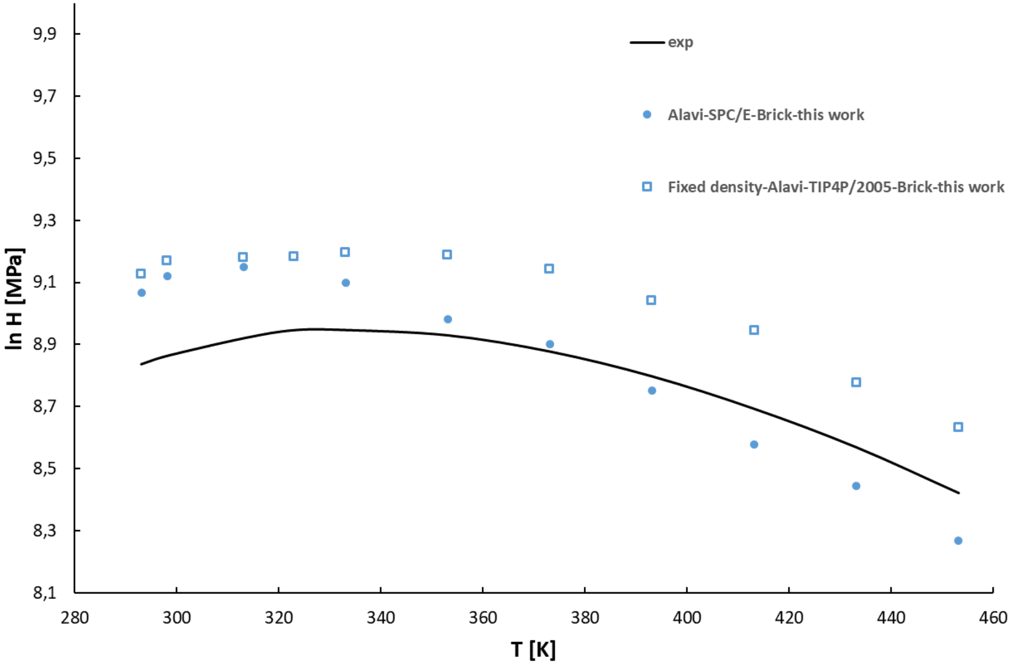


# HENRY COEFFICIENT- H=F(T)

$$\boldsymbol{\rho = f(T)}$$

$$Hi = \rho k_B T \exp(\mu_i^{ex}/k_B T)$$

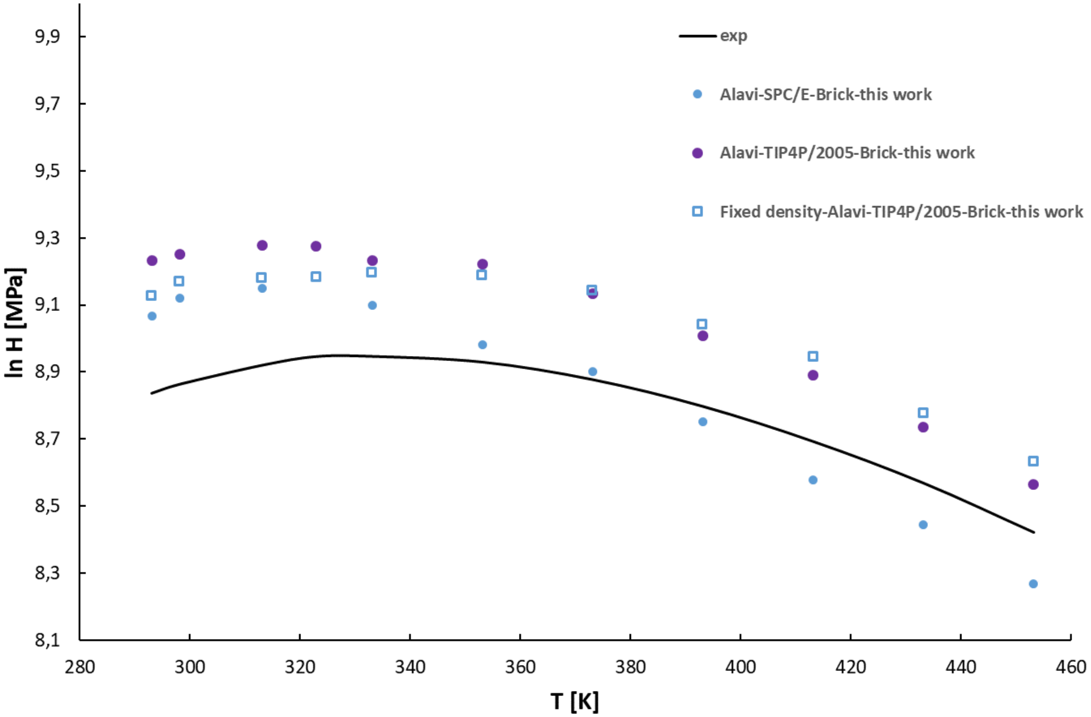


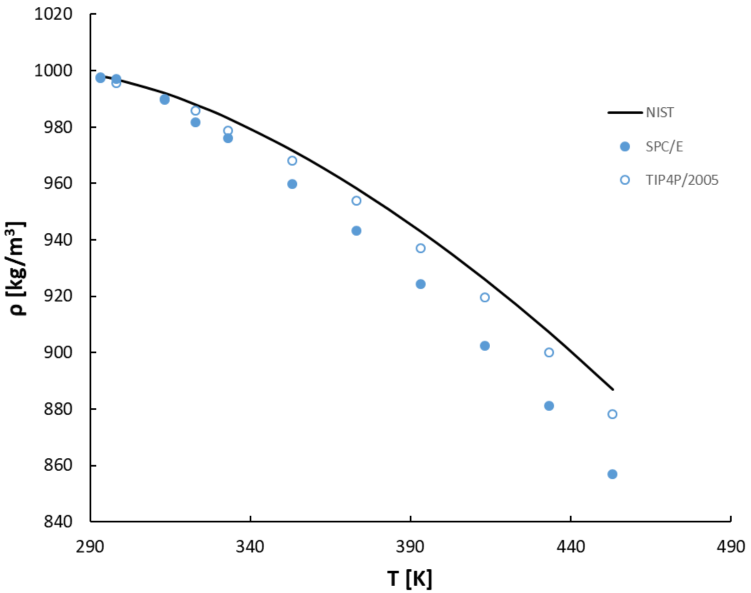


- At high temperature (T>353K), the SPC/E model does not capture well the water density => test a new force field for water: **TIP4P/2005**

# HENRY COEFFICIENT- H=F(T)

Effect of density on the qualitative representation of H vs. T

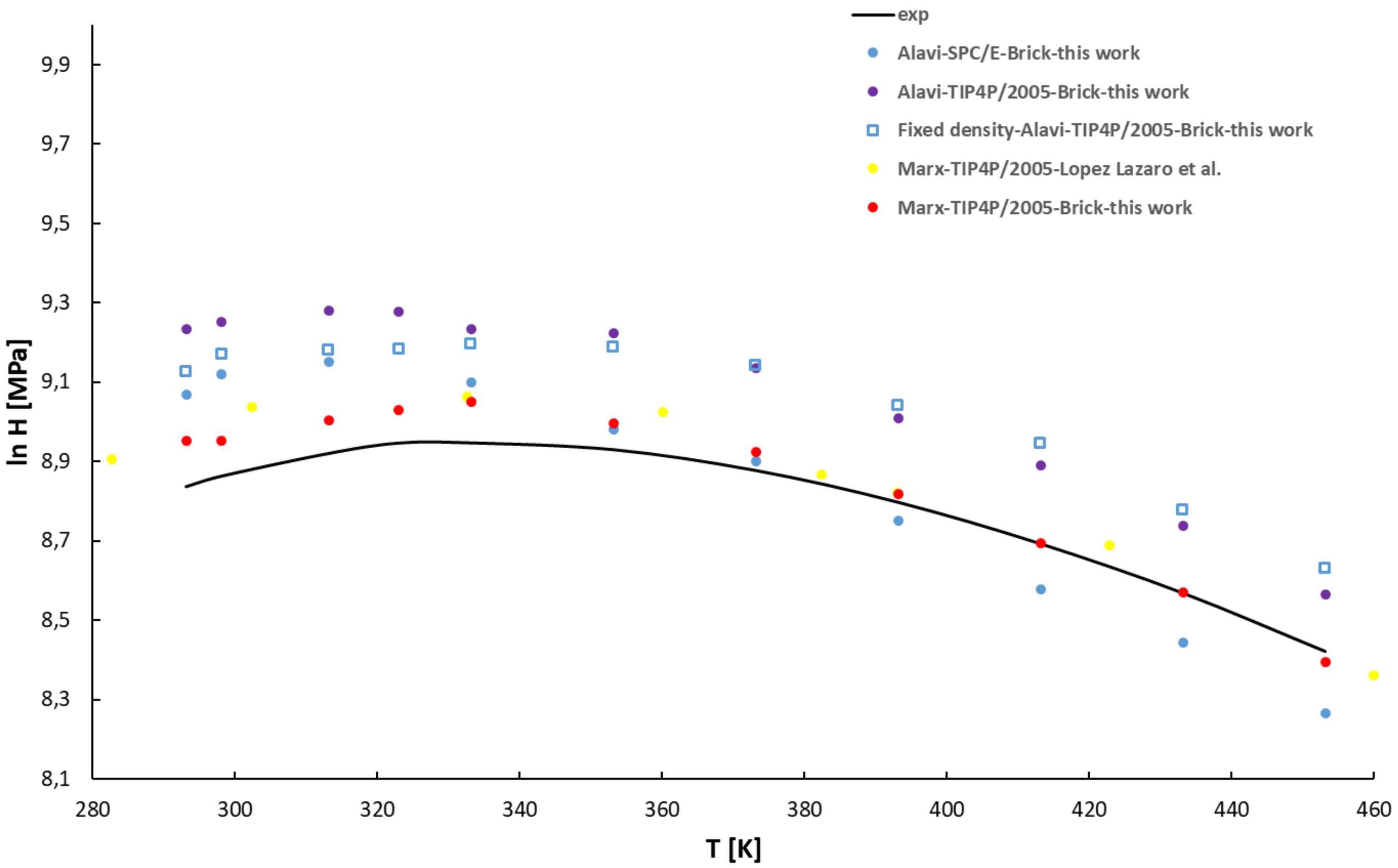




By **fixing the density** (exp) or by **using a suitable model for water density** (TIP4P/2005), the results are **qualitatively** much **improved** (H vs. T)

What can be done to quantitatively improve predictions?

# HENRY COEFFICIENT- H=F(T)



- Using the **Marx** model for $H_2$ (also used by Lazaro et al. 2019, **IFPEN**) significantly **improves** the predictions.

# SOLUBILITY ($x_{H2}$) FROM HENRY COEFFICIENT

$$H_{H_2} = \frac{P*\varphi_{H_2}*y_{H_2}}{x_{H_2}*Poy_{H_2}(P,T)} \quad with:\ Poy_{H_2}(P,T) = \exp(\vartheta^{\infty}_{H_2}\frac{P-P^{sat}}{RT})$$

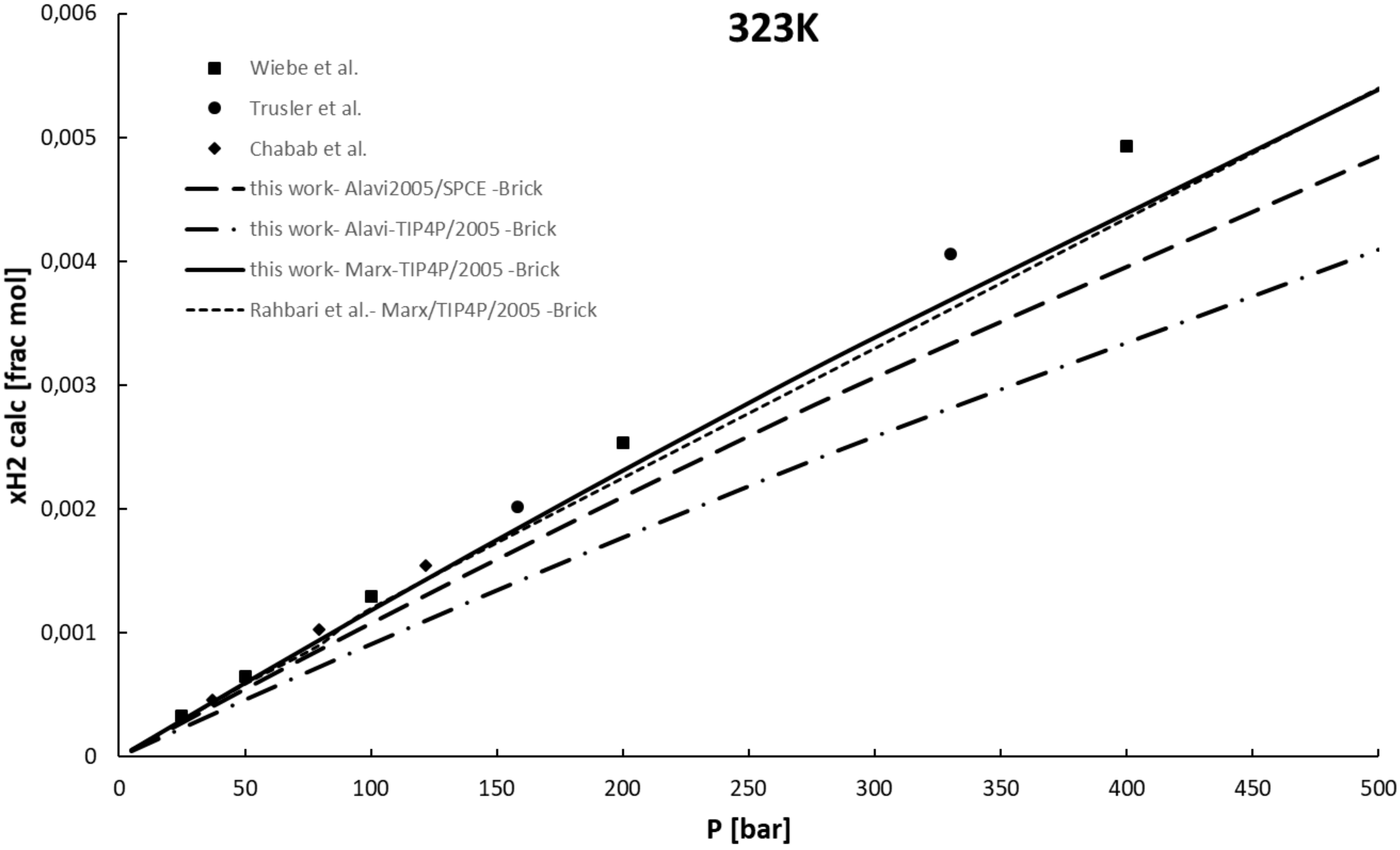
$$x_{H_2} = \frac{P*\varphi_{H_2}*y_{H_2}}{H_{H_2}*Poy_{H_2}(P,T)}$$

**P:** Total pressure
**$\boldsymbol{\varphi_{H_2}}$(T,P):** fugacity coefficient of $H_2$ in the vapor phase
**$\mathbf{y_{H_2}}$:** $H_2$ content in the vapor phase
$\mathbf{Poy_{H_2}(T,P)}$: $Poynting\ factor$
$\boldsymbol{\vartheta^{\infty}_{H_2}}$:partial molar volume of $H_2$ at infinite dilution

$\boldsymbol{\vartheta^{\infty}_{H_2} = f(T)}$, It is assumed that $\vartheta^{\infty}_{H_2} \neq f(P)$

- From the literature (available only at T=298.15° C and P=1 bar)
- From molecular simulation

# SOLUBILITY ($x_{H2}$) FROM HENRY COEFFICIENT



# Thermodynamics modeling of the

# $H_2 + H_2O + NaCl$ system

# THERMODYNAMICS MODELING OF THE $H_2 + H_2O + NaCl$ SYSTEM

## I) Symmetric approach (phi-phi)

Same Equation of State (EoS) for each phase

$$x_i \Phi_i^{Liq} = y_i \Phi_i^{vap}$$

### 1) Soreide and Whitson (SW) EoS

- Peng-Robinson EoS with different BIPs (T and salinity dependent) for liquid and gas phases and a specific alpha-function for brine.
- Recent parameters from ***Chabab** et al. 2021*

### 2) e-PR-CPA EoS

*(ref : **Chabab** et al., 2019)*

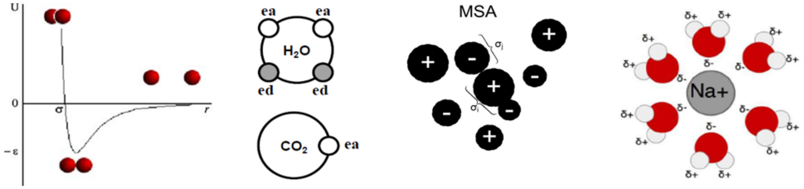
$$\frac{A^{res}_{e-PR-CPA}}{RT} = \frac{A^{PR}}{RT} + \frac{A^{Association}}{RT} + \frac{A^{MSA}}{RT} + \frac{A^{Born}}{RT}$$

Attractive and dispersive interactions

Associative interactions

Long-range interactions

Short-range interactions (solvation)



## II) Asymmetric approach (gamma-phi)

### 3) Using Henry's constant

$$\underbrace{x_i^{aq}\gamma_i^{aq}\mathrm{H}_i^{g}(T,P^{sat})\exp\left(v_i^{\infty}\frac{P-P^{sat}}{RT}\right)}_{\text{Liquid}} = \underbrace{y_i^{g}\varphi_i^{g}}_{\text{Gas}}P$$

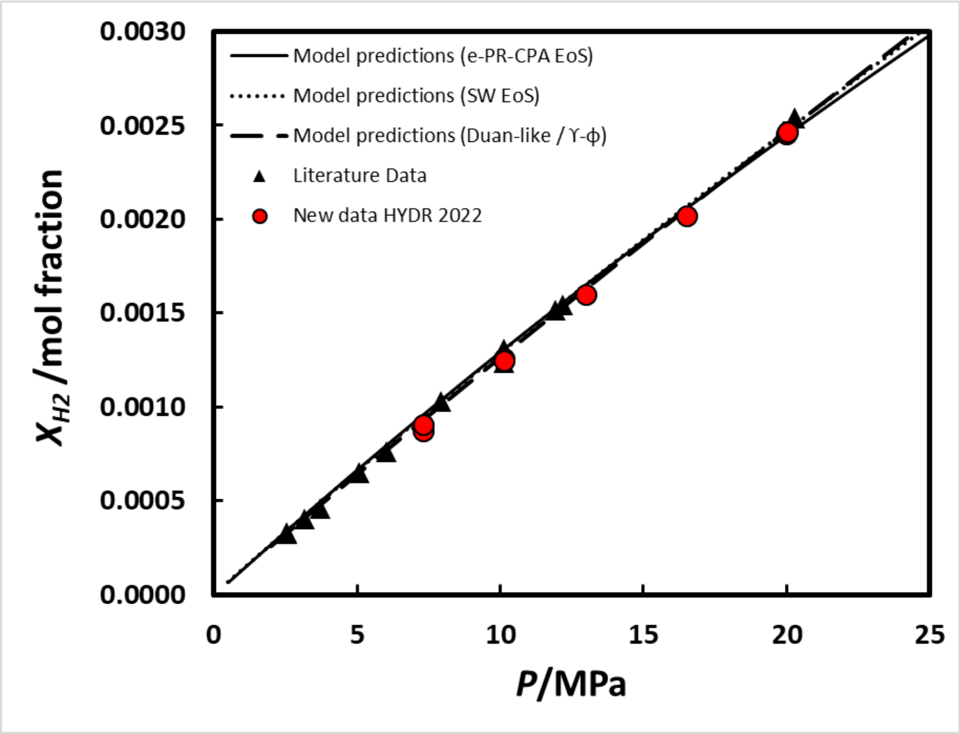
### 4) Duan-type model

$$\underbrace{\mu_i^{l(0)} + RTln(\gamma_i) + RTln(x_i)}_{\text{Liquid}} = \underbrace{\mu_i^{v(0)} + RTln(y_iP) + RTln(\varphi_i)}_{\text{Gas}}$$

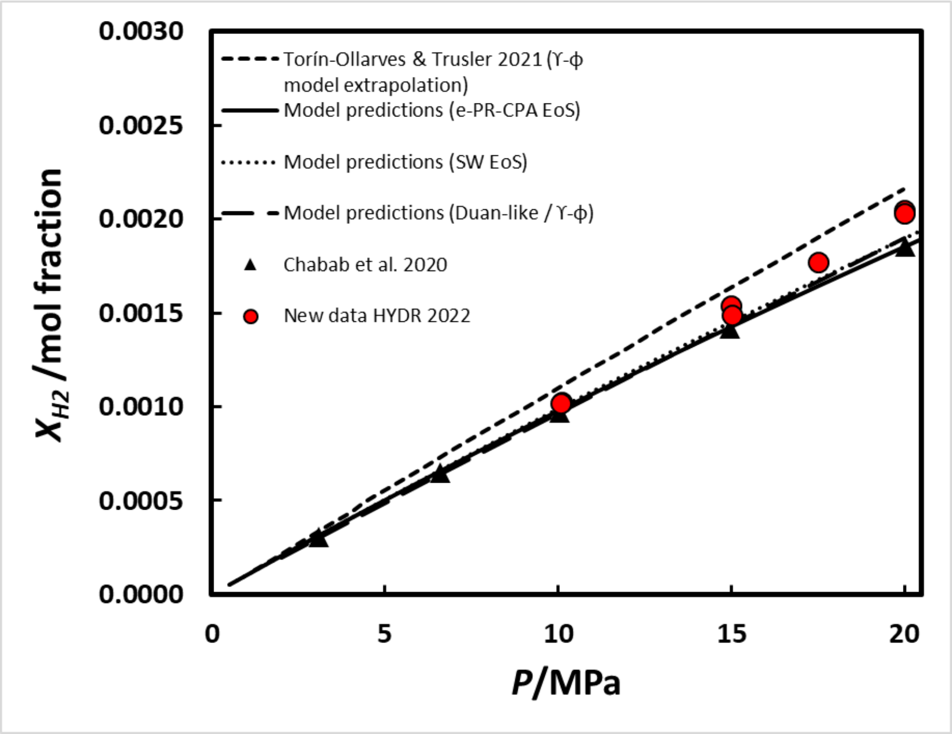
# THERMODYNAMICS MODELING OF THE $H_2 + H_2O$ + NACL SYSTEM

T = 323.15 K

**$H_2 + H_2O$**



**$H_2 + H_2O$ + 1m NaCl**



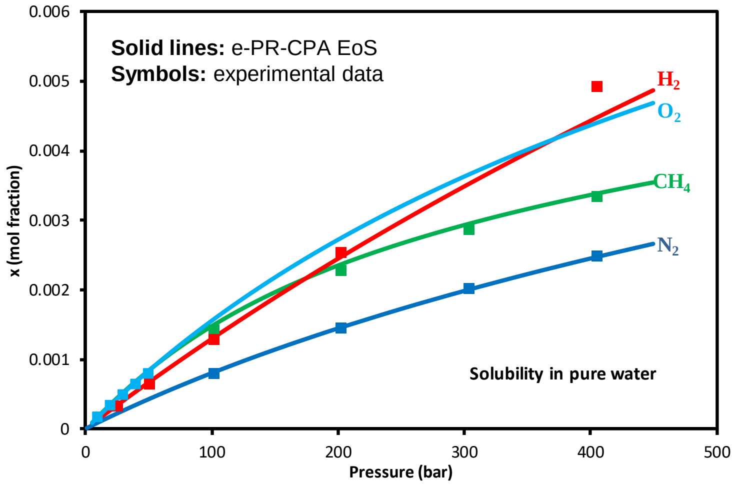
# SOME COMMENTS…

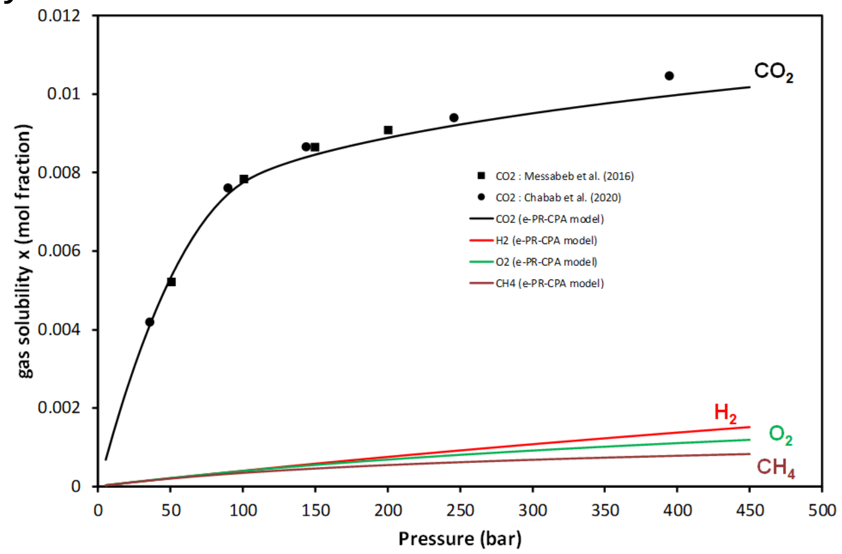
## 1) Salting-out effect of $CH_4$, $N_2$, $O_2$, and $H_2$ in 1m NaCl brine

| | $CH_4$ | $O_2$ | $N_2$ | $H_2$ |
|---|---|---|---|---|
| **100*(1-$x_{\text{in brine}}$/$x_{\text{in water}}$)** | 25.35 | 25.38 | 25.24 | **17.18** **(This work)**<br>12.25 (Torín & Trusler 2021)<br>24.28 (Chabab et al. 2020) |

## 2) Gas solubility dependencies:

- Intermolecular forces (HB, e.g. $CO_2$)
- Coulombic interactions
- Molecule size
- Polarizability





*(To go deeper, see **Battino, R., & Seybold, P. G. (2011). The $O_2$/$N_2$Ratio Gas Solubility Mystery.***

# CONCLUSIONS

**Summary**

- Importance of thermophysical properties for UHS
- Impact of density and chemical potential on solubility prediction (MC simulation)
- Different approaches for the calculation of solubility
- Predictive capacity of MS
- Salting-out effect
- Gas solubility dependencies

**Upcoming work**

- Mixed-gas co-solubility (cushion gas, underground bio-methanation, etc.)
- $H_2$ diffusivity in brine
- Interfacial tension of $H_2$/mixed gas with brine (short/medium term)
- Impact of clay (long term perspective)

# Thank you for your attention!

## Acknowledgements

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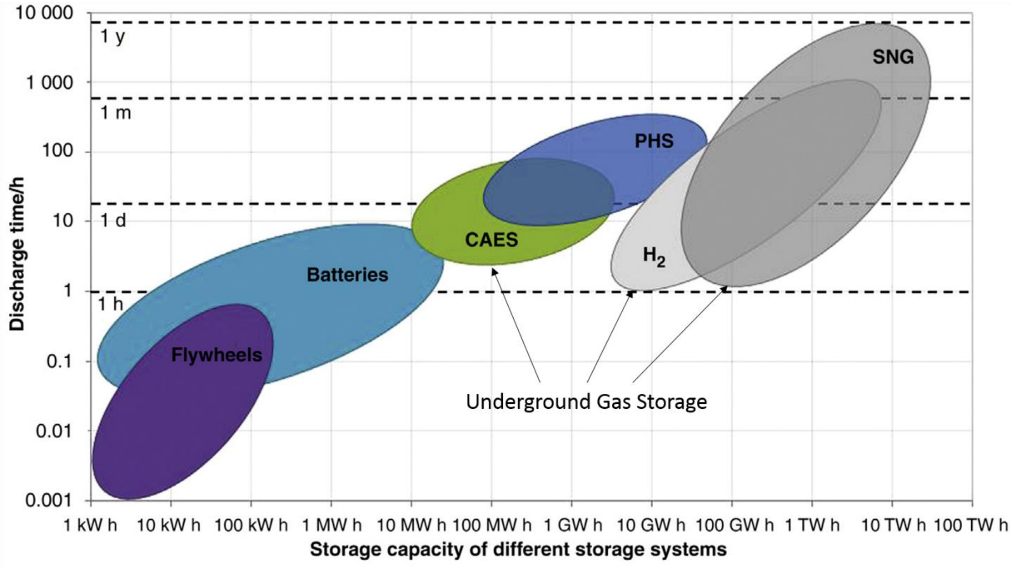
Colleagues from IFPEN
Christophe COQUELET (Mines)

# Additional slides

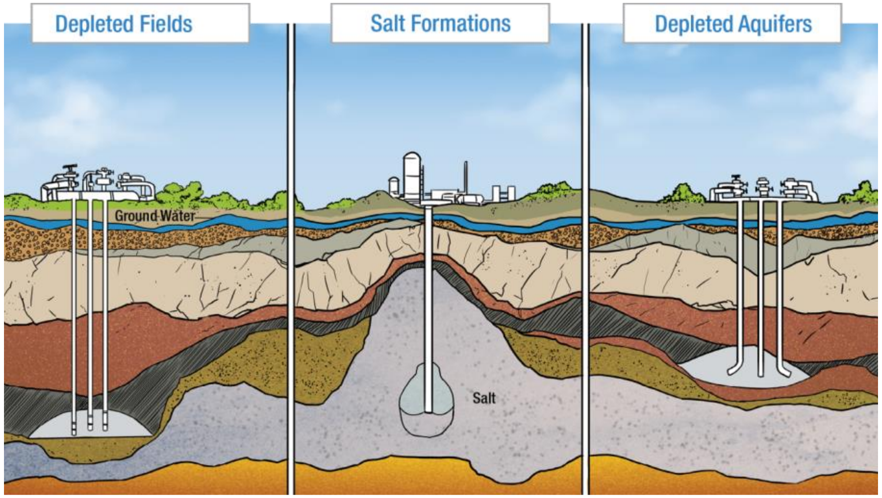
# RESEARCH PROJECT: JUNIOR CHAIR HYDR

## Overview of the different types of energy storage



*Ref : Tichler & Bauer (2016). Power-to-Gas. In Storing Energy.*

## Principal types of underground gas storage



*Ref : J.I.T. Force (2016), Underground natural gas storage: Integrity and safe operations*

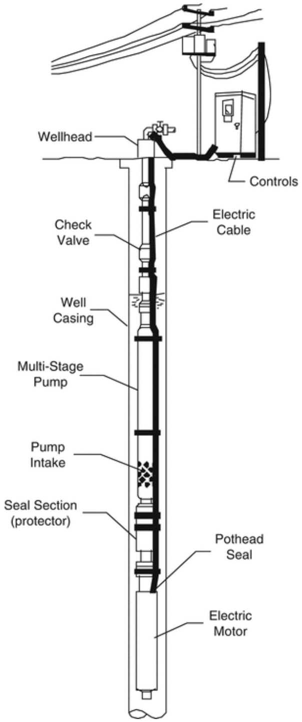
# APPLICATION TO DEGASSING IN GEOTHERMAL PROCESSES

**Effect of degassing in geothermal processes:**

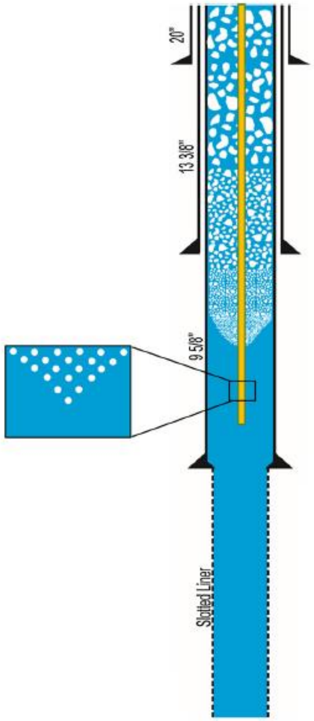
- Reducing the process efficiency
- pH change : salt (e.g., calcite-CaCO3) scaling
- Causing undesired GHG emissions

➢ **Gas breakout depth**

➢ **Working pressure in surface facilities**

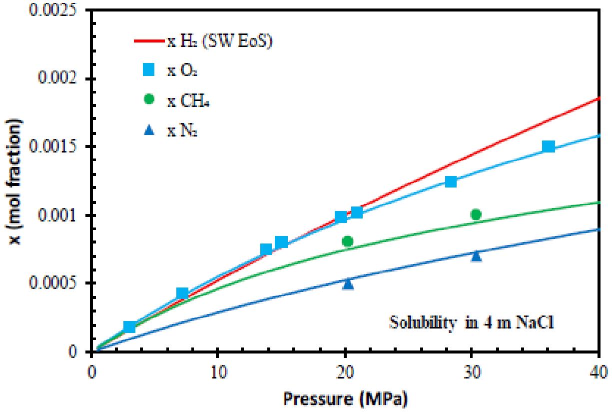


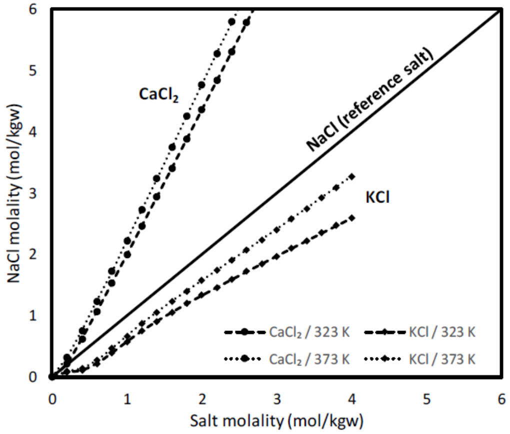
**Submersible pump**

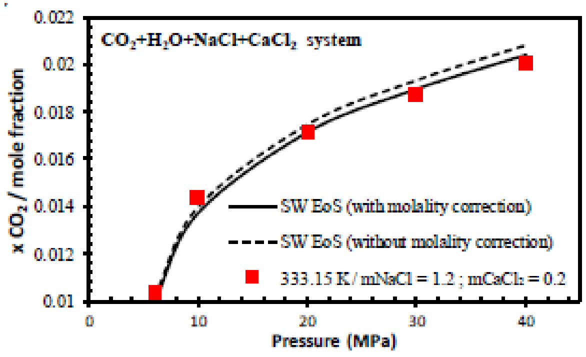


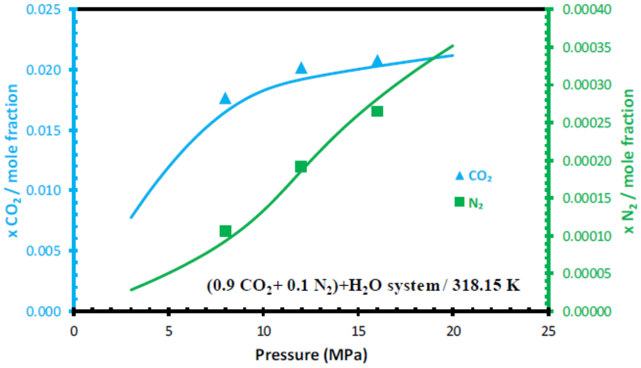
**First gas bubble formation**

# APPLICATION TO DEGASSING IN GEOTHERMAL PROCESSES

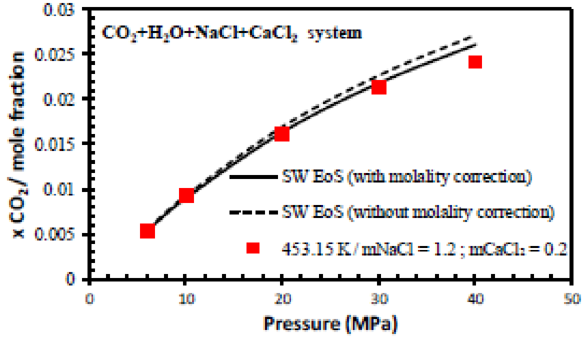




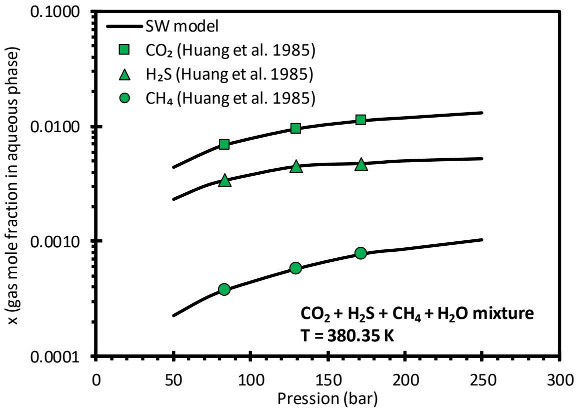




Model : SW EoS with **new** parameters and different salts



- ✓ **Duhring lines** of equal **Gas** solubility in different brines
- ✓ **Mutual Solubilities** of **Gas-Brine (Single** or **Mixed** Salts**)**
- ✓ **Mixed-gas** cosolubility



Ref : 1) Chabab, S et al. (2021). Energies, 14, 5239.
2) Chabab, S et al. (2022). EGC 2022, Berlin.

# APPLICATION TO DEGASSING IN GEOTHERMAL PROCESSES

**Prediction of :**

- ✓ **Bubble-Point Pressure** and
- ✓ **GHG Emission Rate** (g-eqCO2/kWh) in the Upper Rhine Graben **Geothermal Sites**

**Selected models :**

- ❖ **Phase equilibria :** EoS **(Søreide and Whitson)** with **new** parameters
- ❖ **GLR** conversion **: GERG-2008** for **gas, Al Ghafri's** correlation for **brine**

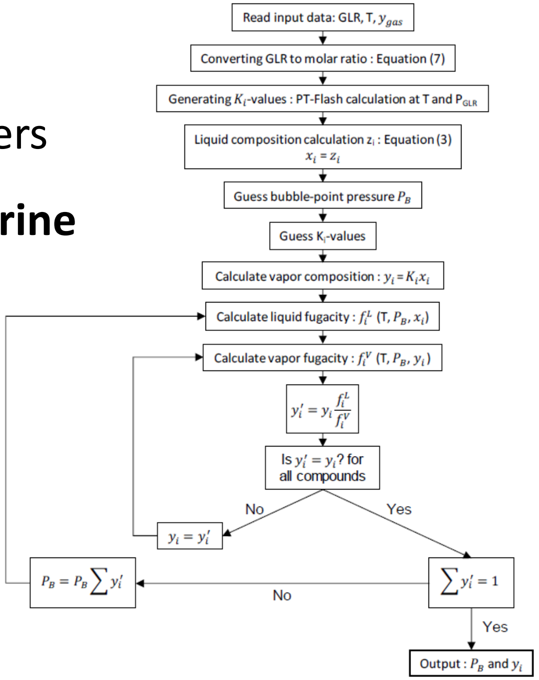
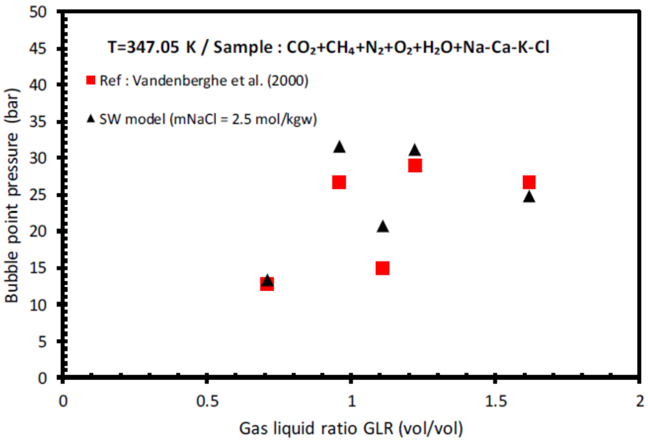
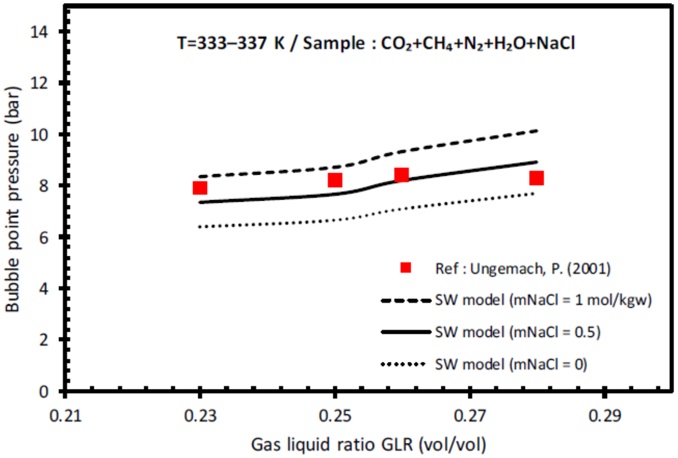


Figure 2. Algorithm for calculating the bubble point pressure of geothermal fluids.





Chabab, S et al. (2021). Energies, 14, 5239.