Thermodynamic and geochemical behavior of salt caverns

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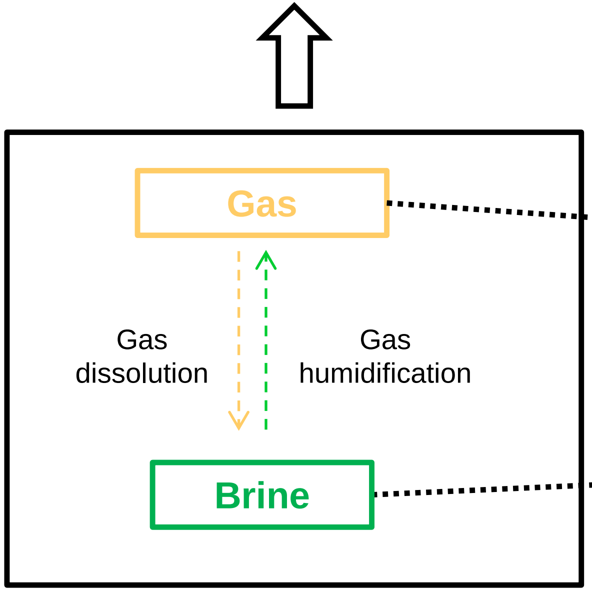
1. Introduction : Context and goals

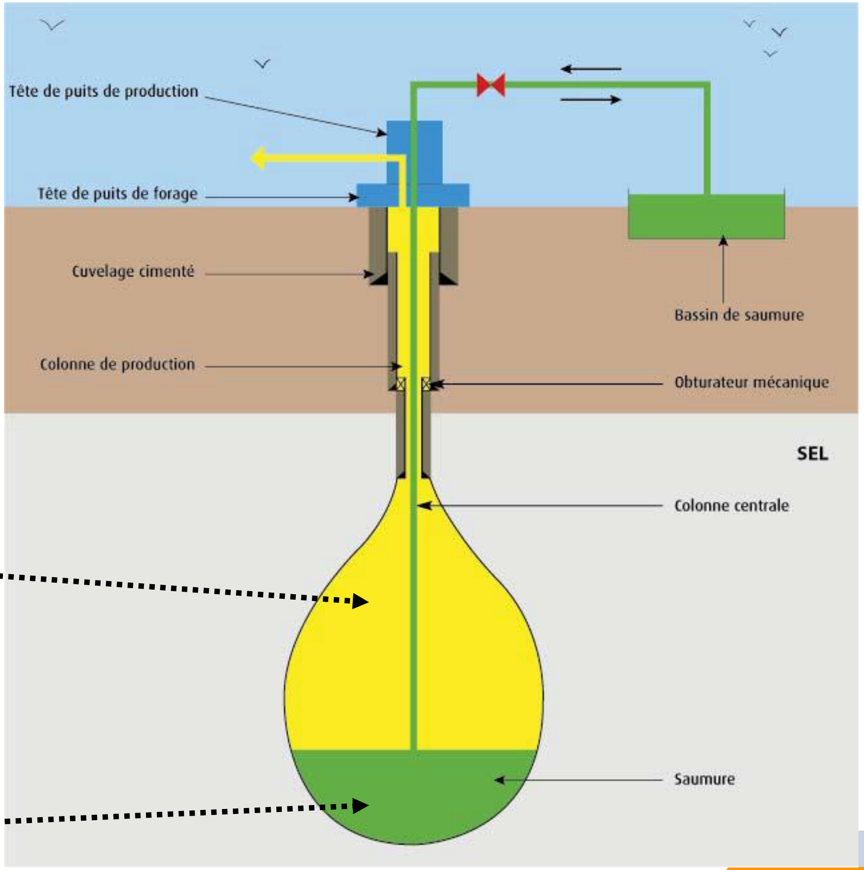
❖Thermophysical properties: ρ, η, IFT

❖gas solubility

❖water content

❖hydrate stability

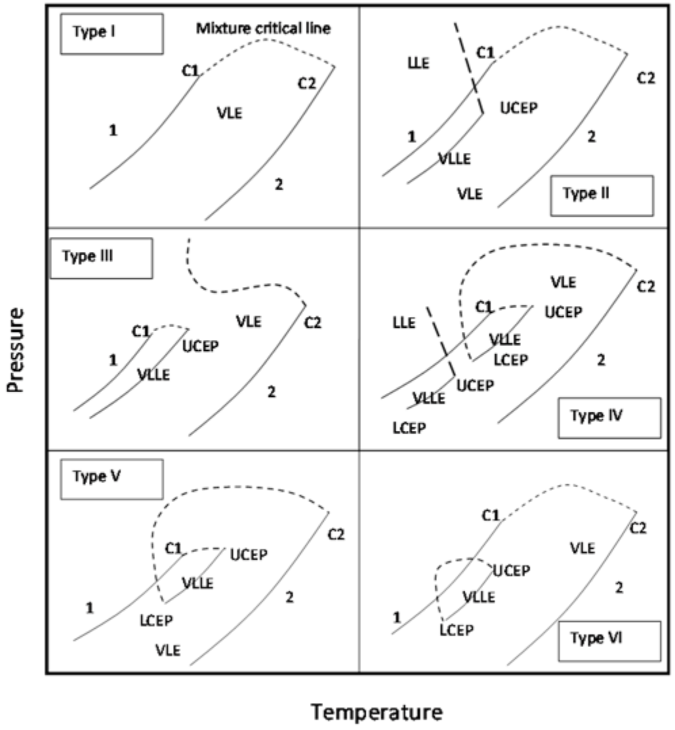


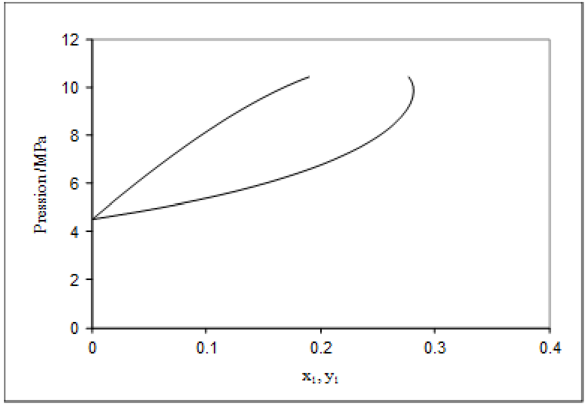


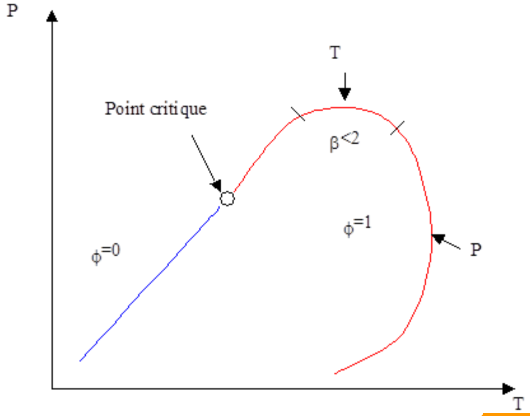
Ref : INERIS N° - DRA-13-133158-12929A

1. Introduction : Phase diagram

○ Van Konynenburg and Scott Classification



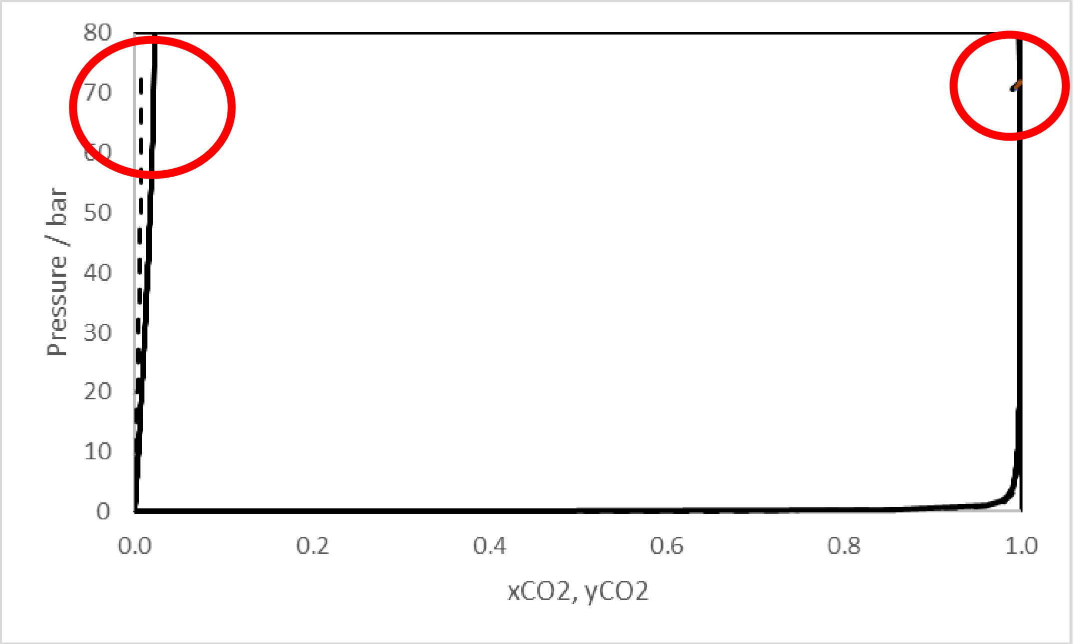




1. Introduction : Phase diagram- Salting out effect

○ Results

Solution with NaCl 4M

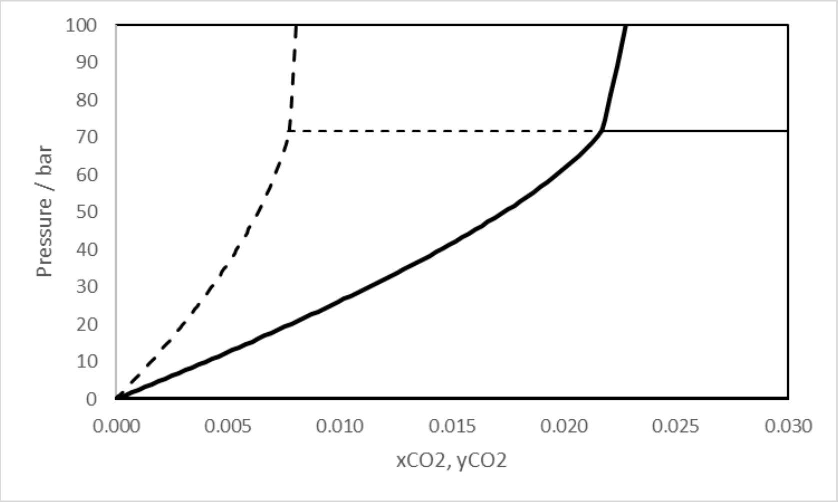


- ❑Peng Robinson + Soreide and Whiston approach
- ❑Comparison with pure water (solid line)
- ❑303.15 K

1. Introduction : Phase diagram- Salting out effect

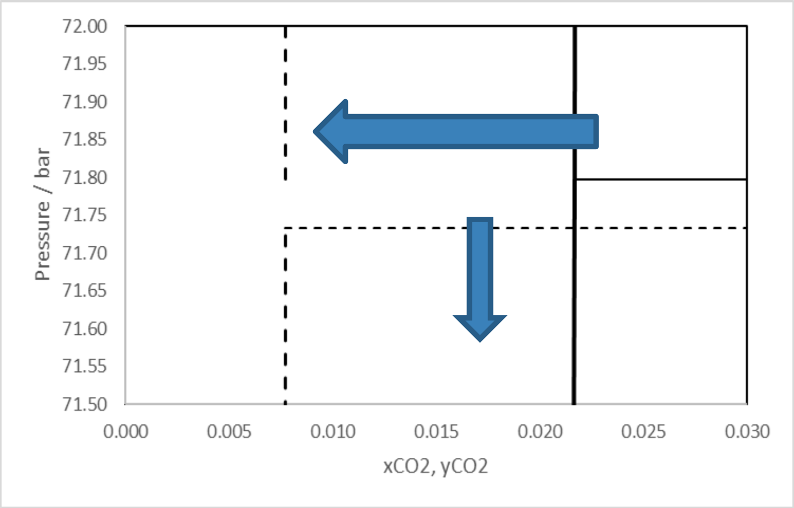
○ Results

Solution with NaCl 4M



Liquid phase

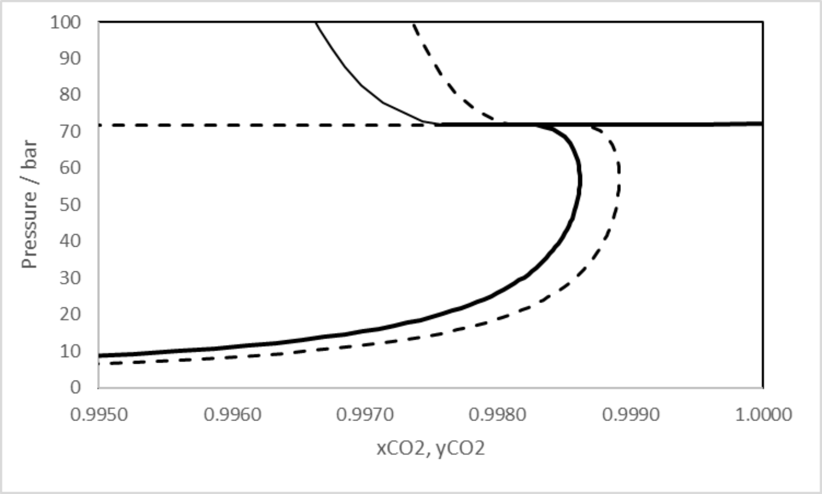
Addition of salt



1. Introduction : Phase diagram- Salting out effect

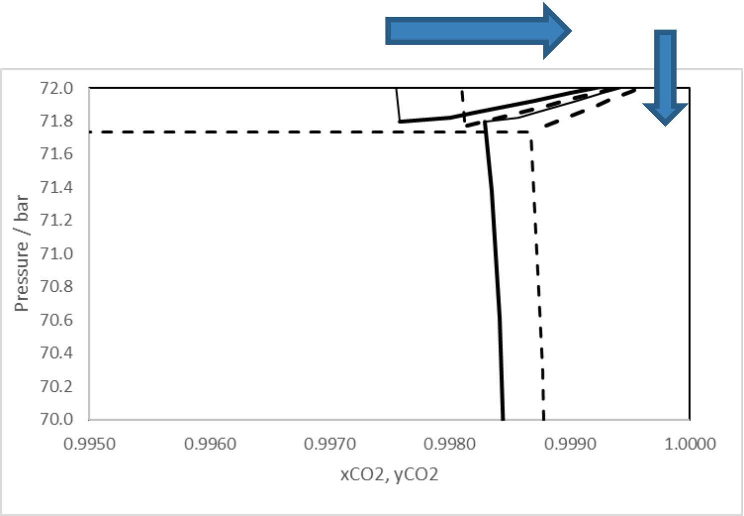
○ Results

Solution with NaCl 4M



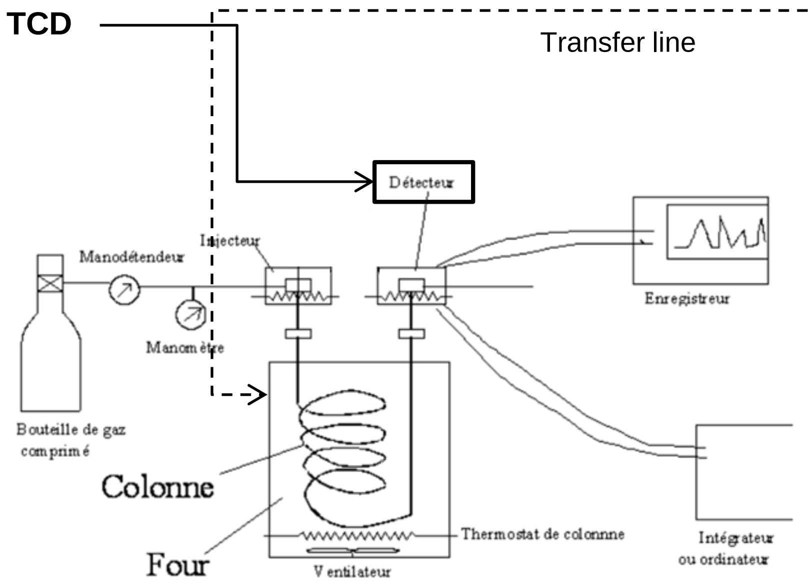
Vapor phase

Addition of salt

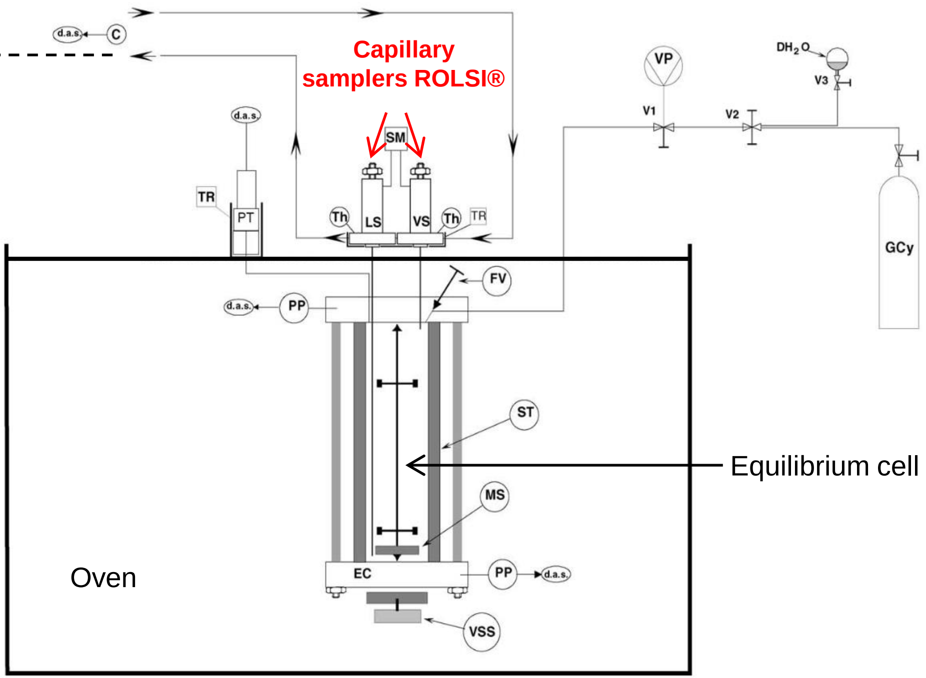


2. Experimental aspects: Equipments

a) Static-analytic setup



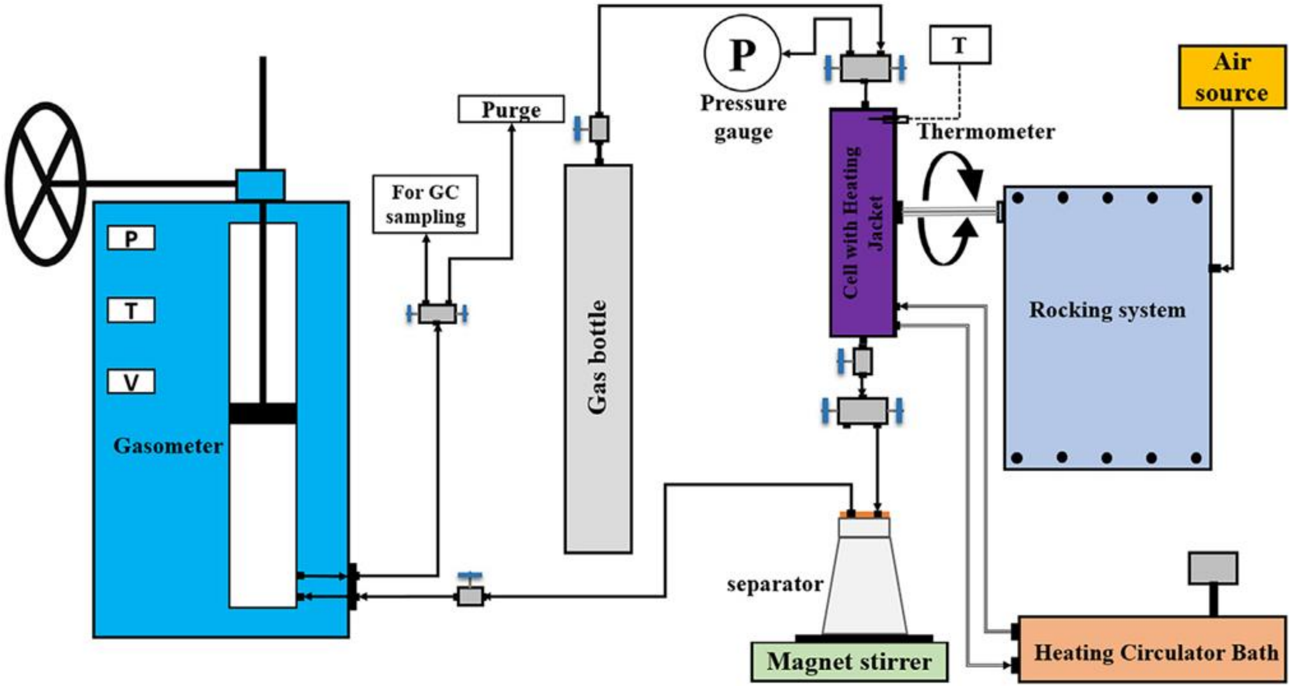
Analysis part (Gas chromatography)



Phase equilibrium part

2. Experimental aspects: Equipments

b) Rocking cell setup (volumetric method)



Ref : Ahmadi and Chapoy 2018

Solubility measurements performed:

- $CO_2 + H_2O + Na^+ + Cl^-$
- $O_2 + H_2O + Na^+ + Cl^-$

3. Modeling: e-PR-CPA – model for electrolyte

- **3.1 PR-CPA model (cubic plus association)**

  2 terms:

  - **Cubic EoS**: Peng – Robinson (Peng et Robinson, 1978)
  - **Association term from** Wertheim's theory (Wertheim, 1984)

$$P = \underbrace{\frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}}_{\text{PR EoS}} - \underbrace{\frac{1}{2}\frac{RT}{v}\left(1+\rho\frac{\partial \ln(g)}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1-X_{A_i})}_{\text{Wertheim's term}}$$

$$a_i = a_{c,i} \times \left[1 + m_i\left(1-\sqrt{\frac{T}{T_{c,i}}}\right)\right]^2 \qquad a_{c,i} = \Omega_a \frac{R^2 T_{c,i}^2}{P_{c,i}} \qquad b_i = \Omega_b \frac{RT_{c,i}}{P_{c,i}}$$

X_{A_i} monomer fraction:

$$X_{A_i} = \frac{1}{1+\rho\sum_j x_j \sum_{B_j} X_{B_j}\Delta^{A_iB_j}}$$

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)\right] b_{ij}\beta^{A_iB_j}$$

$$g(\rho) = \frac{1}{1-1.9\left(\frac{1}{4}b\rho\right)}$$

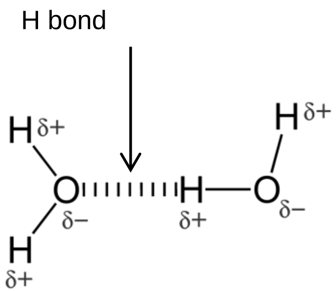
For water, m_i, $a_{c,i}$ and b_i parameters are adjusted on experimental data: vapor pressure and liquid densities.

3. Modeling: e-PR-CPA – model for electrolyte

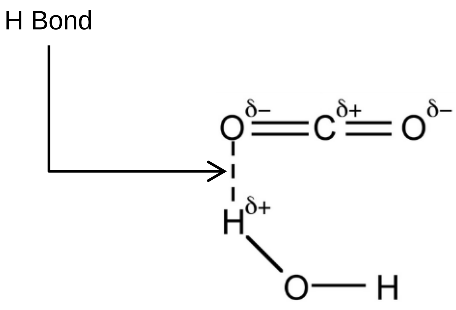
- **3.1 PR-CPA model (cubic plus association)**

Associating term:

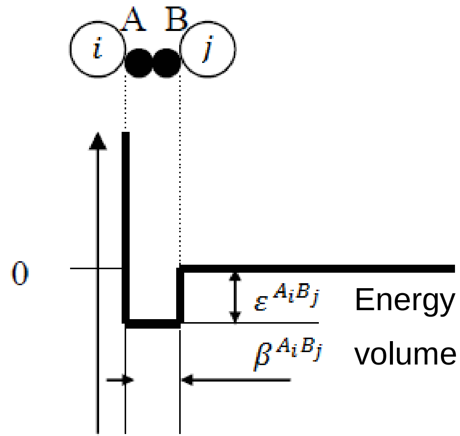
- ➢ Self-association (between two identical molecules)
- ➢ Cross Association (between two different molecules)



Self association (ref : wikimédia)



Solvation (Cross Association)



$\varepsilon^{A_iB_j}$ Energy of association

$\beta^{A_iB_j}$ volume of association

ref : Chapman et al., 1990

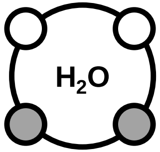
Mixing rules CR1 :

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \qquad \beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}}$$

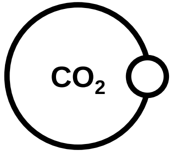
For water, ε and β parameters are adjusted on experimental data: pure component vapor pressure and liquid densities.

3. Modeling: e-PR-CPA – model for electrolyte

- **3.2 Application of PR-CPA model to CO_2-H_2O binary system**



➢ H_2O : 4 sites of association (type 2ed–2ea (4C)), two sites electron donnor and two sites electron acceptor



➢ CO_2 : Solvation and one site electron acceptor (type 0ed–1ea)

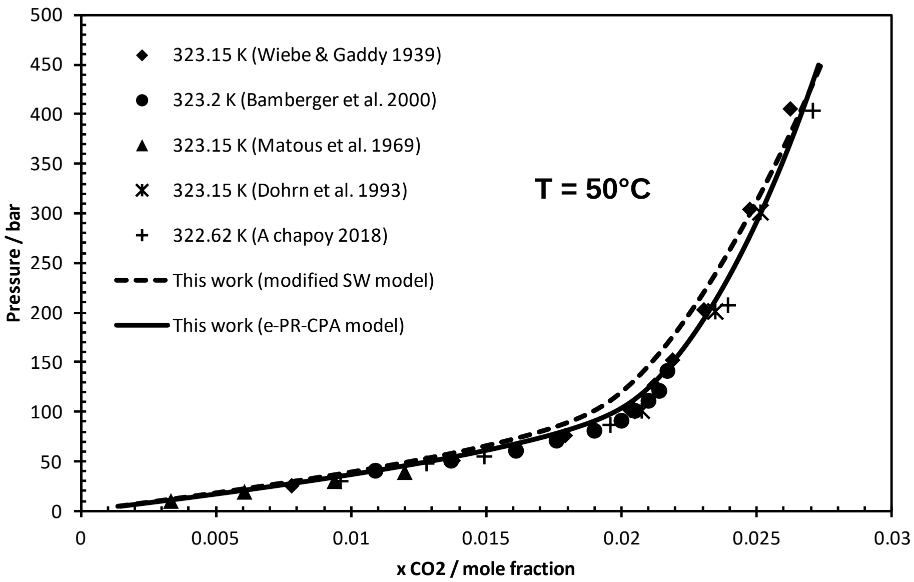
ed : electron donnor

ea : electron acceptor

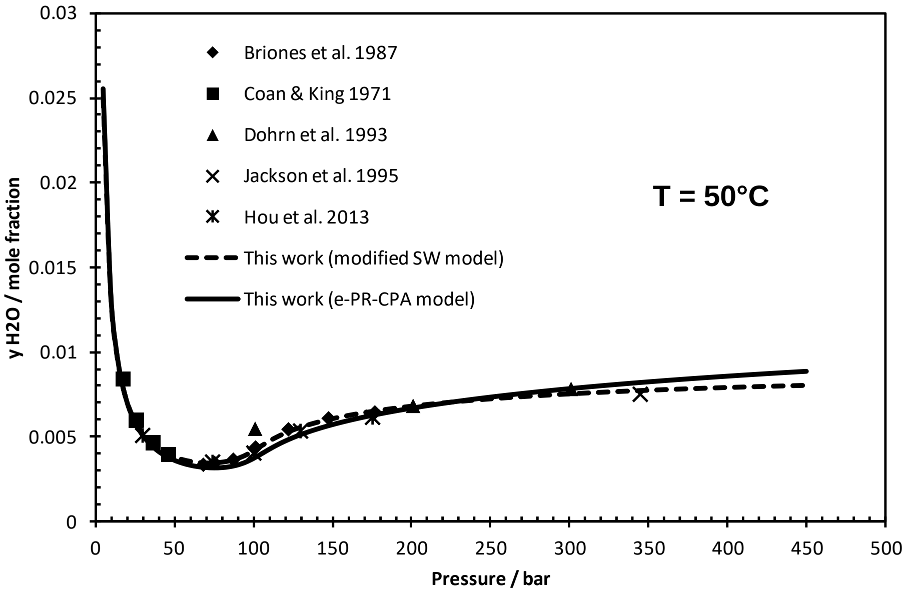
3. Modeling: e-PR-CPA – model for electrolyte

- **3.2 Application of PR-CPA model to CO_2-H_2O binary system**

CO$_2$ solubility in pure water (x_{CO2})



Water content(y_{H2O})



	T min (K)	T max (K)	P min (bar)	P max (bar)	**x AAD %**	**y AAD %**
e-PR-CPA	274.15	473.15	1	700	**5**	**10**
m-SW	274.15	473.15	1	700	**7**	**8**

3. Modeling: e-PR-CPA – model for electrolyte

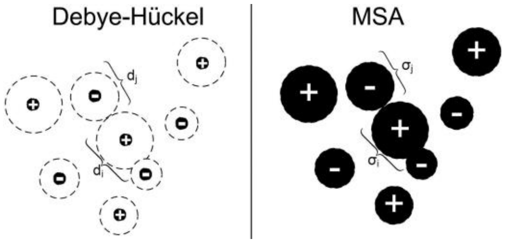
- **3.3. Extension to electrolytes (e-PR-CPA)**

$$A^{e-PR-CPA} = \underbrace{A^{\#}}_{\text{GP}} + \underbrace{A^{PR} + A^{Assoc}}_{\text{PR-CPA}} + \underbrace{A^{E}}_{\text{Electrolyte term}}$$

$$A^{E} = A^{MSA} + A^{Born}$$

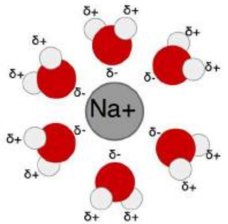
– MSA term (Mean Spherical Approximation: long range interaction

$$\frac{A^{MSA}}{RT} = -\frac{N_{Av}e^2}{4\pi D_0 DRT}\sum_i \frac{n_i Z_i^2 \Gamma}{1+\Gamma\sigma_{b,i}^{MSA}} + \frac{V\Gamma^3}{3\pi N_{Av}}$$



– Born term: short range interaction (solvation)

$$\frac{A^{Born}}{RT} = -\frac{N_{Av}e^2}{4\pi D_0 RT}\left(1-\frac{1}{D}\right)\sum_i \frac{n_i Z_i^2}{\sigma_{b,i}^{Born}}$$



Thermodynamic properties from $A^{e\text{-}PR\text{-}CPA}$

$$P = -RT\left(\frac{\partial\left(\frac{A^r}{RT}\right)}{\partial V}\right)_{T,n} + \frac{nRT}{V}$$

$$\ln(\varphi) = \left(\frac{\partial\left(\frac{A^r}{RT}\right)}{\partial n_i}\right)_{T,V} - \ln(Z)$$

Other properties (Michelsen & Mollerup 2004)

3. Modeling: e-PR-CPA – model for electrolyte

- **3.4. Parametrisation of e-PR-CPA model**

Parameters for each ion: m_i, $a_{0,i}$ and σ_i

$$a_i(T) = a_{0,i}\left[1 + m_i\left(1 - \sqrt{\frac{T}{298.15}}\right)\right]^2 \qquad b_i = \frac{N_{Av}\pi\left(\sigma_{b,i}^{hs}\right)^3}{6}$$

Binary interaction parameters: $K_{H_2O-anion}$,$K_{H_2O-cation}$ et$K_{cation-anion}$

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

Which kind of properties for the adjustment of each parameters(H_2O+ions) ?

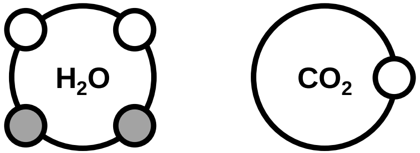
-**Vapor Pressure**
-Liquid densities at sat
} Equilibrium properties

-MIAC*
-**Osmotic coeffcient**
} Excess properties

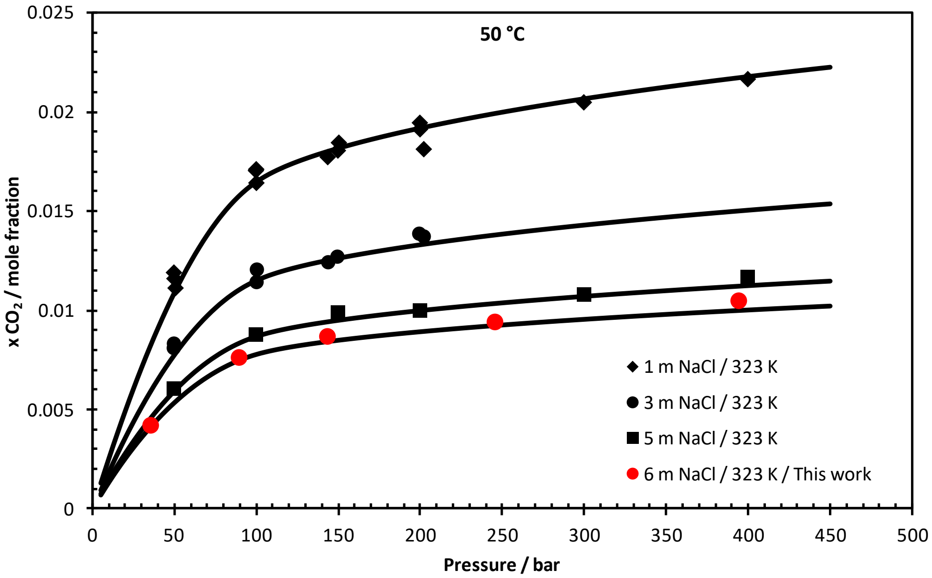
*MIAC = mean ionic activity coefficient

4. Experimental results and modeling

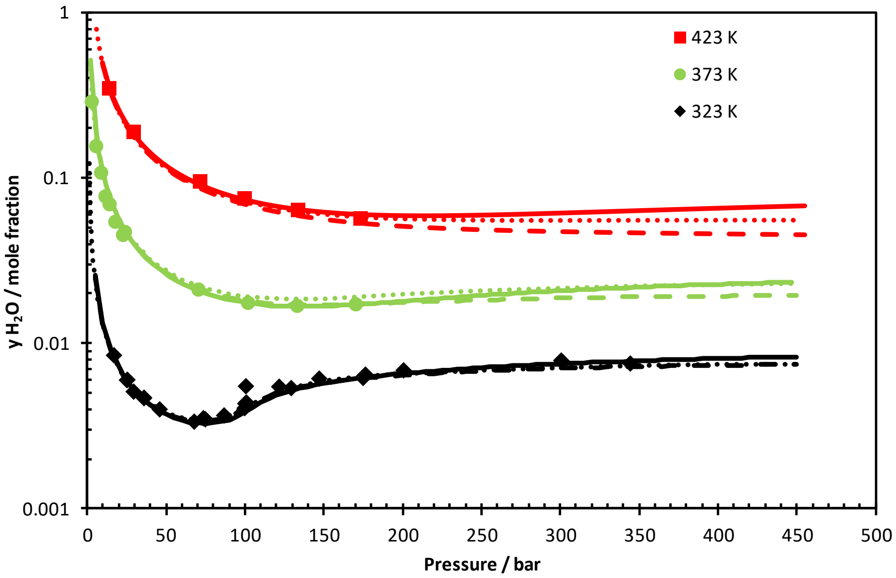
- **4.1. Application of e-PR-CPA model to $CO_2 + H_2O + Na^+ + Cl^-$ system**



Solubility of CO_2 in H_2O + NaCl



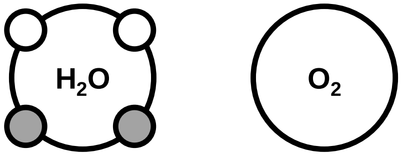
Water content in the $CO_2 + H_2O$ system



Chabab, S., Théveneau, P., Corvisier, J., Coquelet, C., Paricaud, P., Houriez, C., & El Ahmar, E. (2019). Thermodynamic study of the CO2–H2O–NaCl system: Measurements of CO2 solubility and modeling of phase equilibria using Soreide and Whitson, electrolyte CPA and SIT models. International Journal of Greenhouse Gas Control, 91, 102825.

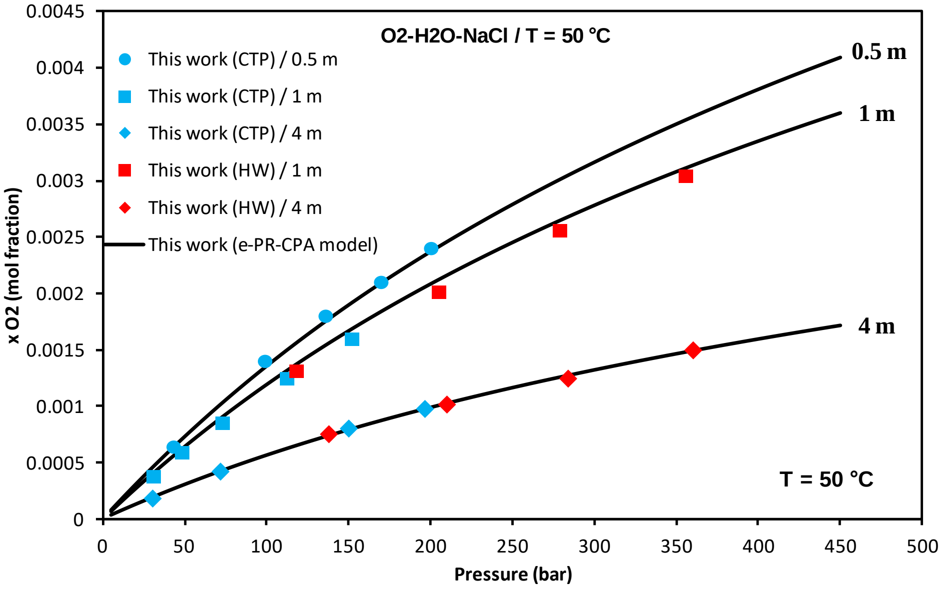
4. Experimental results and modeling

- **4.2. Application of e-PR-CPA model to $O_2 + H_2O + Na^+ + Cl^-$ system**

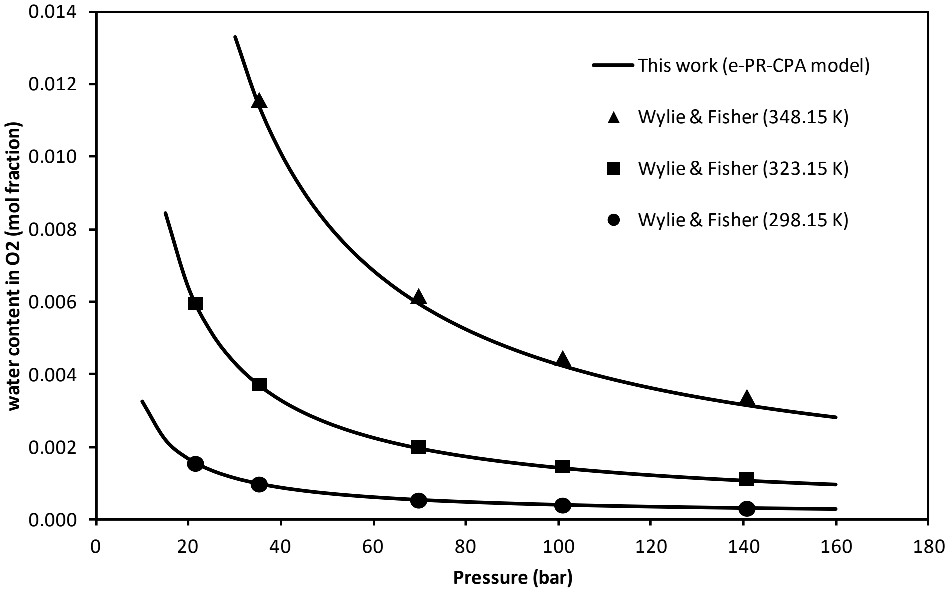


No solvation

Solubility of O_2 in H_2O + NaCl

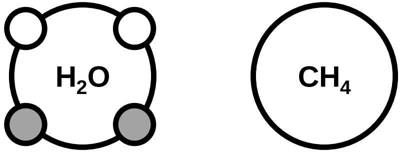


Water content in the $O_2 + H_2O$ system



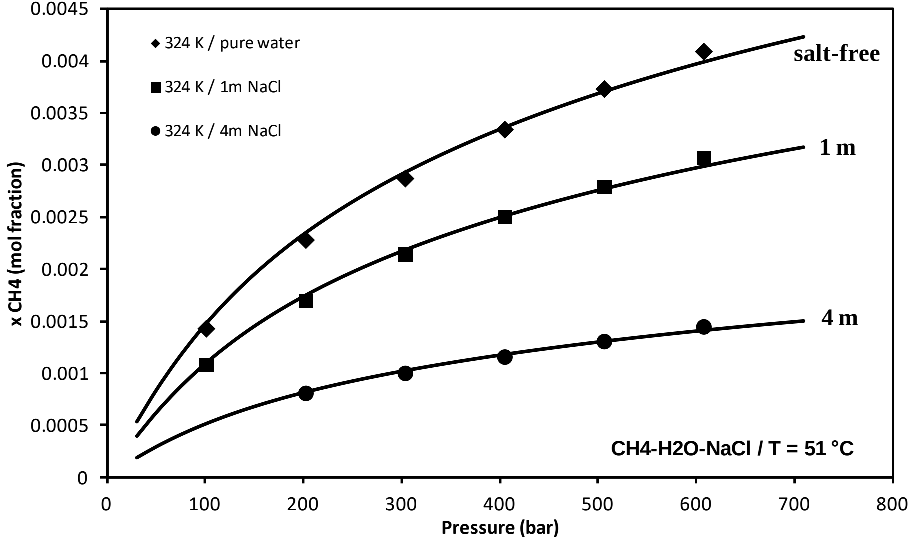
4. Experimental results and modeling

• **4.3. Application of e-PR-CPA model to $CH_4 + H_2O + Na^+ + Cl^-$ system**

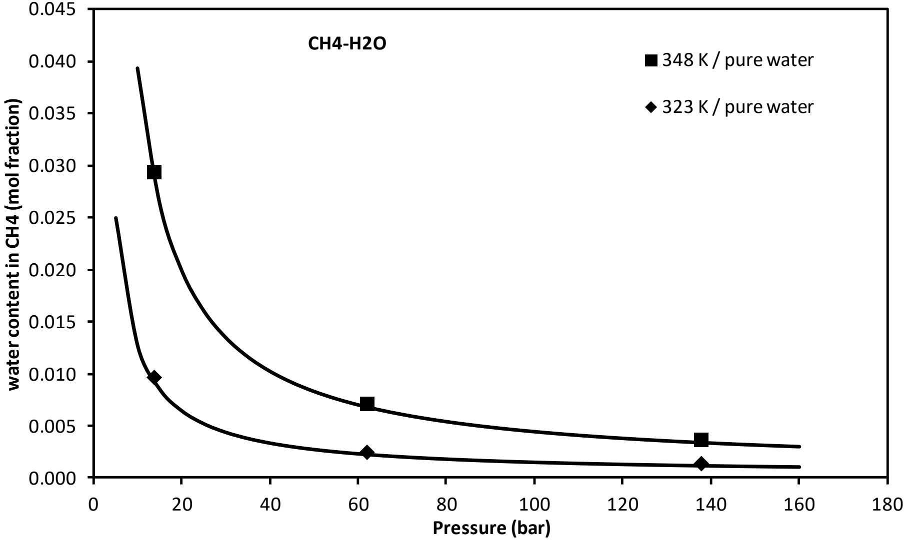


No solvation

Solubility of CH_4 in H_2O + NaCl



Water content in the $CH_4 + H_2O$ system



5. Geochemical modeling

No reactivity with **salts** but **potential reactivity** with

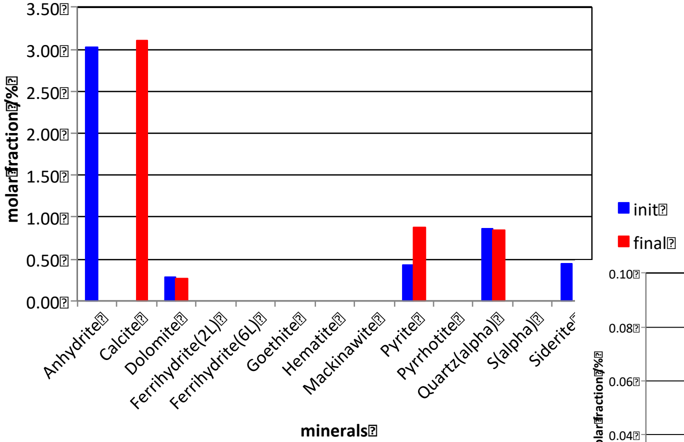
- **insolubles (sulfates…)** $CH_4 + SO_4^{2-} \rightarrow H_2S + CO_3^{2-} + H_2O$
- **well materials (cement…)** $CO_2 + Ca^{2+} + OH^- \rightarrow CaCO_{3(s)} + H^+$

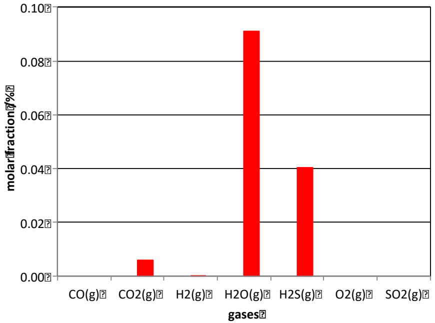
Impact on stored gas quality

Impact on storage sealing

Development of a **geochemical heterogeneous model** using **PR EOS** (gas) and **SIT** (electrolyte)

Reactivity induced by CH_4

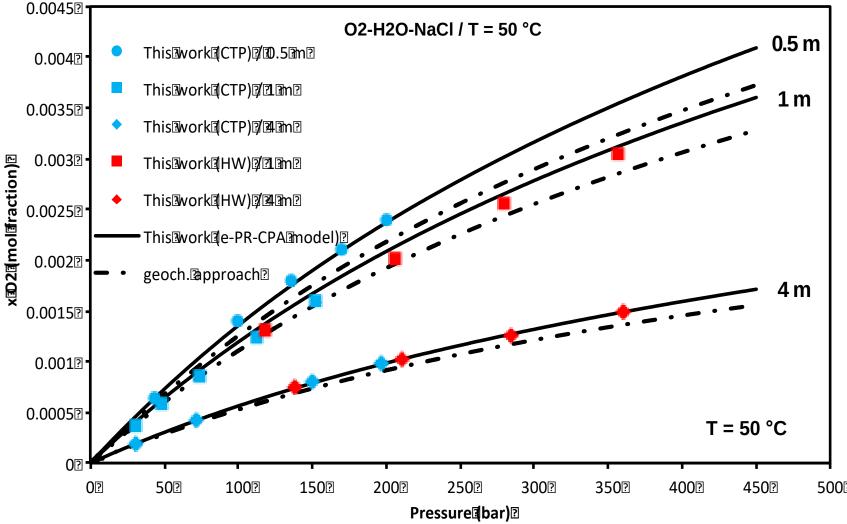




Anhydrite → Calcite + Pyrite

$CH_{4(g)} \rightarrow H_2S_{(g)} + CO_{2\ (g)}$

Solubility of O_2 in H_2O + NaCl



Conclusion

- Importance of thermodynamic properties
- Complexity of phase diagram
- Effects of T, P and salinity (salting out effect) perfectly known
- Development of new equipment for phase equilibrium measurements
- Solubility of CO_2, O_2 and CH_4 determined
- Comparison of two models for the data treatment and the representation of phase diagrams

Acknowledgements

ANR and partners of FLUID Story project

<u>CTP team</u>

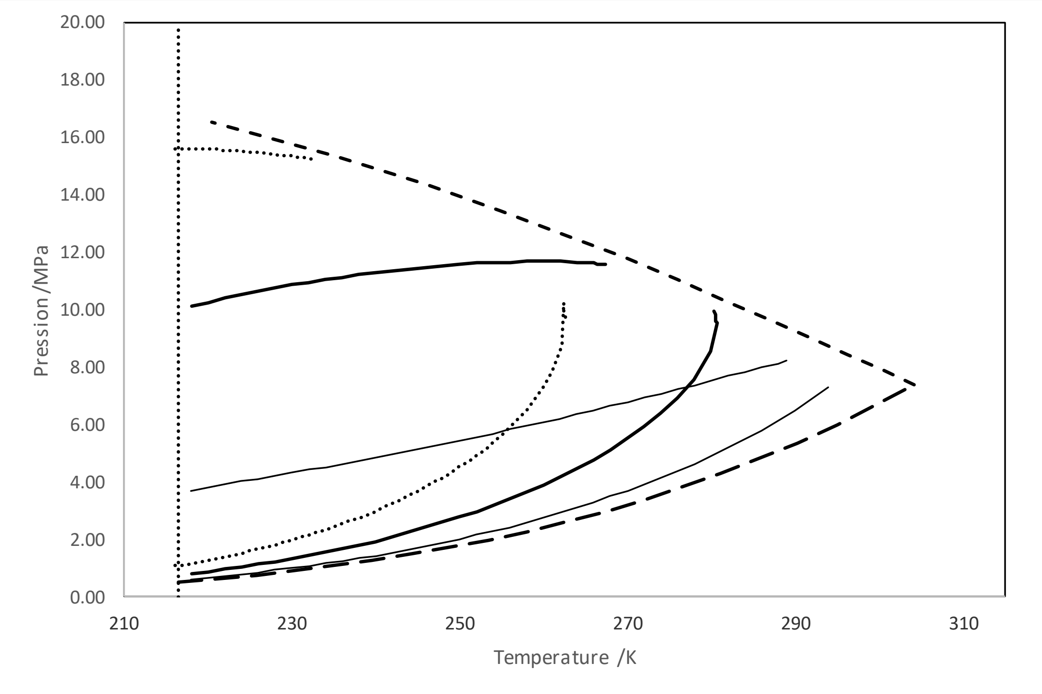
Alain Valtz, Snaide Ahamada, CTP Workshop

<u>Heriot Watt University team</u>

Pr. Antonin Chapoy

Additional slides

○ Results

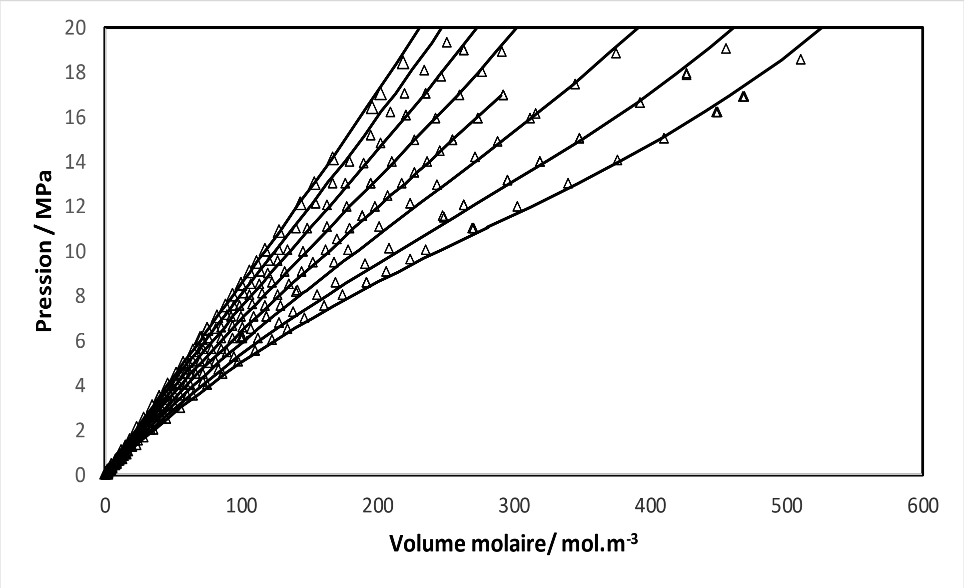


O_2	CO_2
0.1	0.9
0.3	0.7
0.5	0.5

PT Envelop binary system CO_2 + for 3 compositions. Dashed line : Pure CO_2 vapor pressure. Dotted line: mixture critical point line. Vertical line : melting temperature of CO_2.

1. Introduction : Phase diagram- densities

- Results



Pressure molar volume diagram of O_2 (0.5) + CO_2 (0.5) binary system at 230, 250, 270, 290, 310, 370 and 400 K. Symbol: experimental data (vibrating tube densitometer)

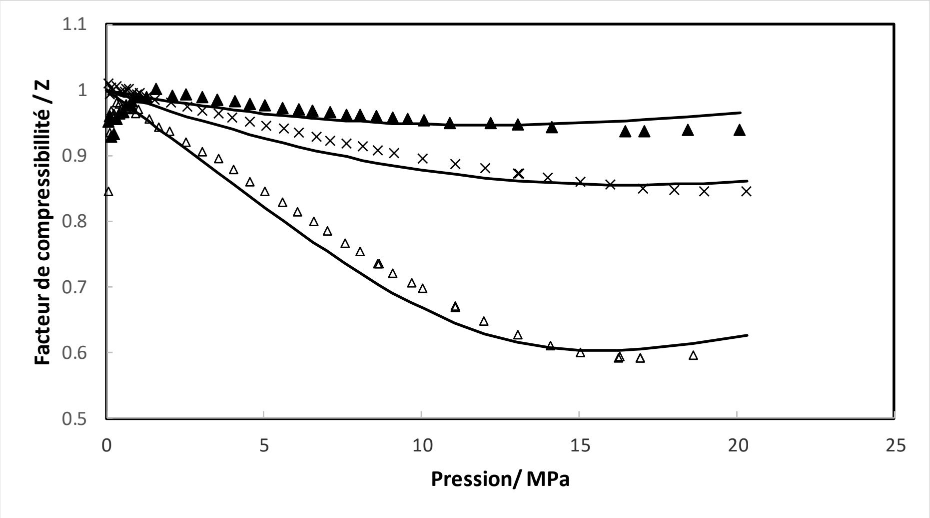
Comparison with EoS prediction (PR EoS) using parameters fitted on VLE data

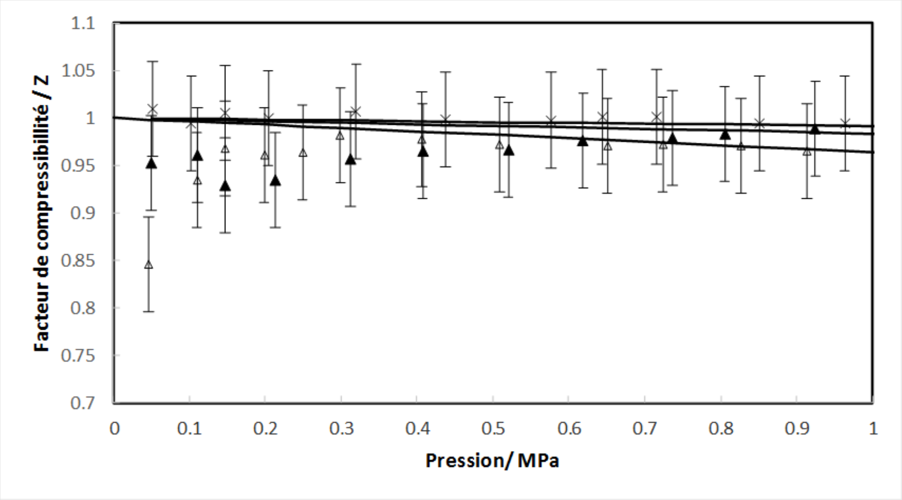
Analysis of compressibility factor

1. Introduction : Phase diagram- densities

○ Results

Good evolution of compressibility factor (see results at 120 deg C)





Z=1 if p->0

Gas hydrate prediction (e-PR-CPA model)

Prediction of gas hydrate phase diagram for the CO_2 + O_2 binary system