

First Principles Thermodynamic Modeling of Phase Change in Dense Phase CO₂ Environment

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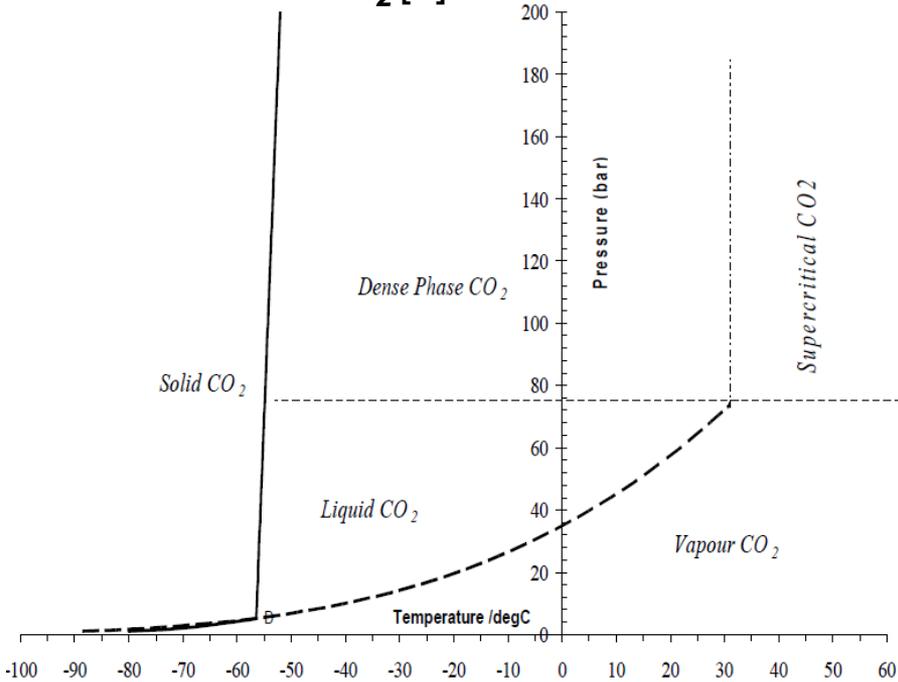


Research Goals

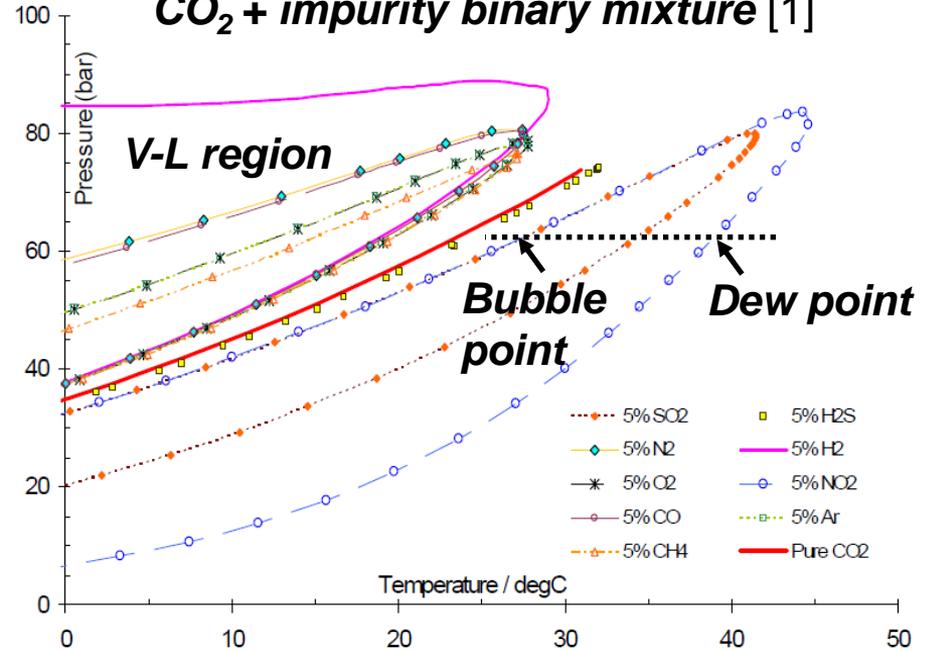
- Develop a thermodynamics-based model that predicts mutual solubilities of water/acid in CO₂ (supercritical/liquid/vapor) in presence of trace impurities.
 - We will employ in-house as well as published experimental data for model development
- Employ molecular simulations to study the homogeneous and heterogeneous nucleation of water (on metal surface or around impurities) in dense phase CO₂ conditions.

Effect of Impurities on the Phase Diagram of CO₂

Pure CO₂ [1]



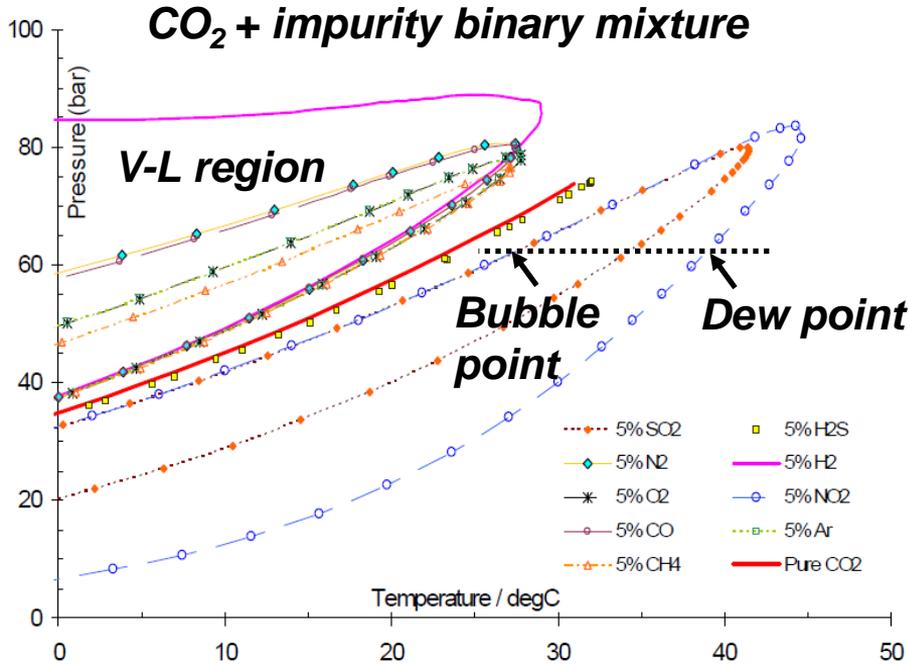
CO₂ + impurity binary mixture [1]



Gibbs phase rule: $DoF = N - \delta + 2$
 N : # species, δ : # phases

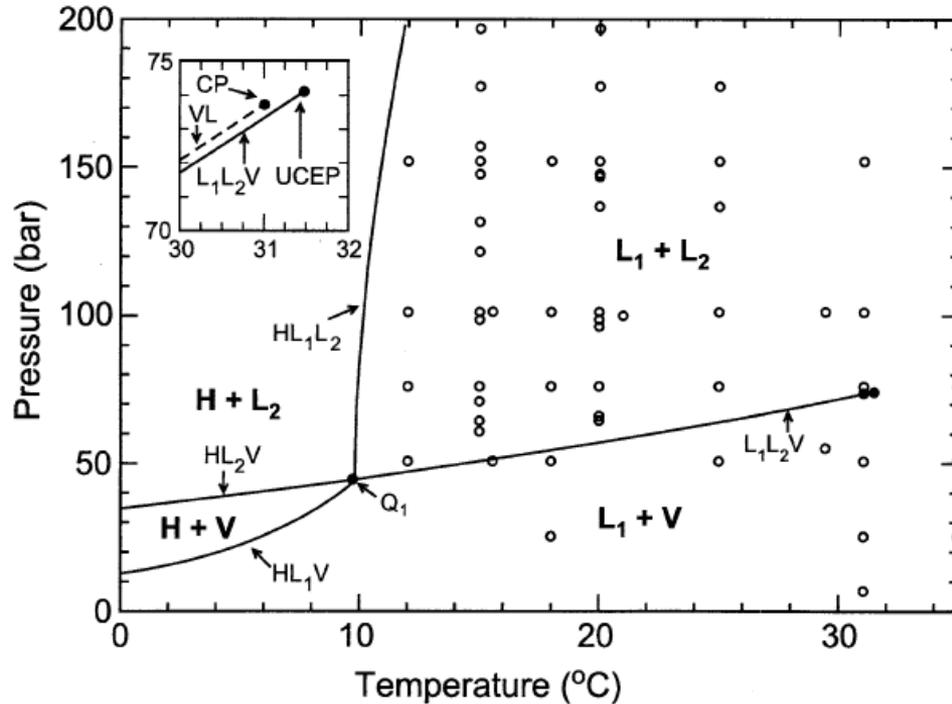
[1] P. N. Seevam, J. M. Race, M. J. Downie, P. Hopkins, International Pipeline Conference (2008), 39 – 51.

Definitions



- **Dew point:** When the first drop of liquid phase appears
- **Bubble point:** When the first bubble of vapor phase appears
- Composition of any phase point in the V-L envelope is determined by the **Lever rule**

Water - CO₂ Phase Diagram [1]



L₁ : Water – rich liquid
L₂ : CO₂ – rich liquid
V : Vapor phase
H : Hydrates

[1] N. Spycher, K. Pruess, J. Ennis-King, Geochimica et Cosmochimica Acta, 67 (2003), 3015 - 3031.

For our purposes, we mainly focus on 2 phase regions

Why? We have trace amounts of impurities in CO_2 or CO_2 + water phase

- **Case 1:** Water condensing out of supercritical (Sc) CO_2 : the two phases are Sc CO_2 and liquid water.
- **Case 2:** Two phase sub-critical CO_2 system: water partitions between the two phases.
- **There is a small three phase region:** Liquid CO_2 , liquid water and vapor CO_2 but if the quantity of water is small, the three-phase region will not be observed.

Gibbs Phase Rule

- Degrees of Freedom (DoF) = $N - \delta + 2$

Where N: # species, δ : # phases

- DoF: number of thermodynamic variables to be specified to define a phase point completely
- Suppose $N = 3$, $\delta = 2$, DoF = 3, which can be (T, x_1, x_2) or (T, P, x_1)
- Suppose $N = 5$, $\delta = 2$, DoF = 5, which can be (T, x_i) or (T, P, x_1, x_2, x_3)

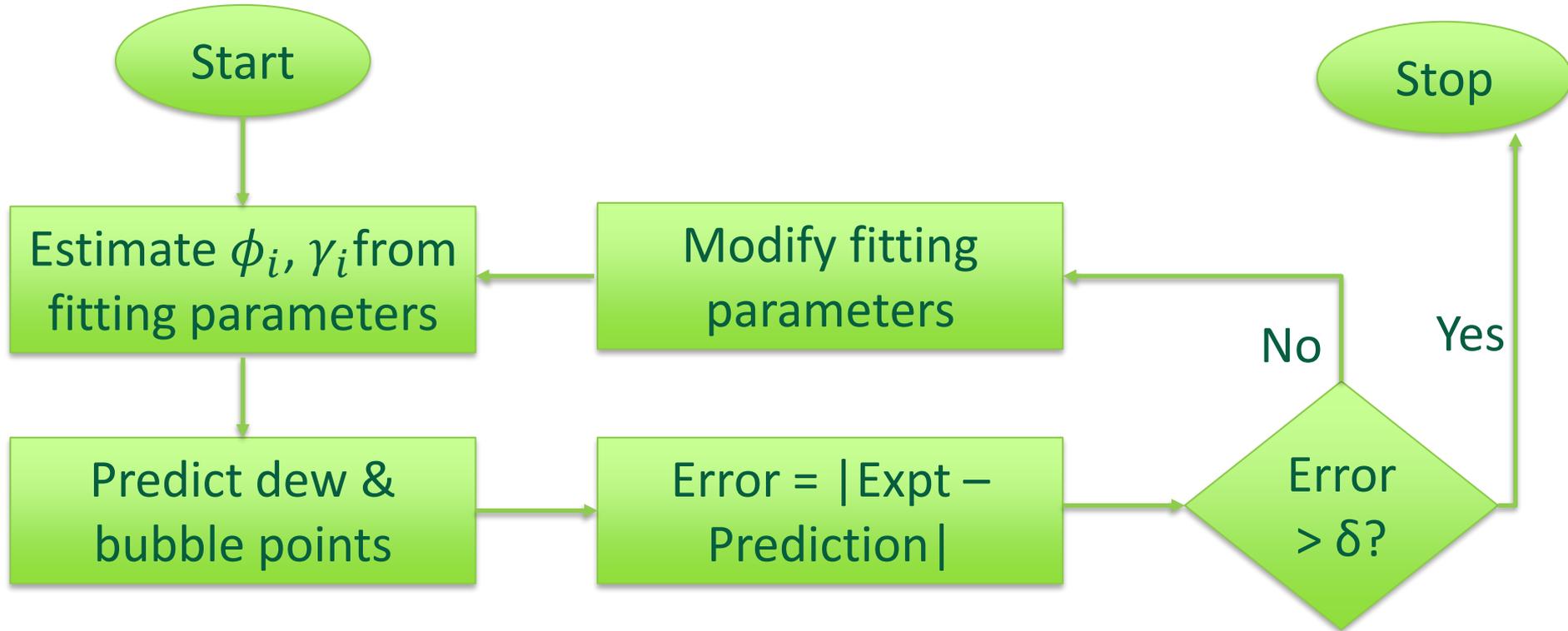
Thermodynamics of Phase Equilibria

- At equilibrium, chemical potential of each species, μ_i in different phases is equal.

$$\mu_i^{liq} = \mu_i^{vap}$$

- Phase equilibrium between an ideal vapor/gas and ideal liquid is described by Raoult's law
- **Overall goal** is to model the non-idealities in the liquid and vapor/gas phases
- Non-idealities are represented as deviations from ideal vapor/gas and ideal (Lewis) liquid
 - Fugacity coefficients for vapor/gas phase: ϕ_i^{vap}
 - Activity coefficients for liquid phase: γ_i^{liq}
- Non-idealities arise from intermolecular interactions. They are system-dependent and are modeled via equation of state and excess Gibbs free energy models

Workflow



Thermodynamics of Phase Equilibria

- At equilibrium, chemical potential of each species, μ_i in different phases is equal.

$$\mu_i^{liq} = \mu_i^{vap}$$

- Define fugacity f_i : $f_i = x_i P \exp\left(\frac{\mu_i - \mu_i^{ig}}{RT}\right)$

- It can be shown that, equivalently, at equilibrium: $f_i^{liq} = f_i^{vap}$

- Define fugacity coefficient:

$$\phi_i^{vap} = \frac{f_i^{vap}}{y_i P}$$

- Define activity coefficient:

$$\gamma_i^{liq} = \frac{f_i^{liq}}{x_i f_i^{pure,liq}}$$

(y_i, x_i : mole fractions of species i in vapor and liquid phases respectively)

Thermodynamics of Phase Equilibria

$$f_i^{pure,liq} \approx P_i^{sat}$$

(Ignoring the Poynting correction factor.
Can be added for high pressures)

- **At V-L equilibrium:** $x_i P_i^{sat} \gamma_i^{liq} = y_i P \phi_i^{vap}$
- **At L-L equilibrium:** $x_i^{liq1} \gamma_i^{liq1} = x_i^{liq2} \gamma_i^{liq2}$
- Phase equilibrium calculations boil down to estimating γ_i^{liq} and ϕ_i^{vap}

Estimating Activity Coefficients

- γ_i^{liq} is related to excess Gibbs free energy, g^E :
$$RT \ln(\gamma_i^{liq}) = \left(\frac{\partial N g^E}{\partial N_i} \right)_{T,P}$$

Mixed Solvent Electrolyte Model [1,2,3]

$$g^E = g_{LR}^E + g_{MR}^E + g_{SR}^E$$

Long range
electrostatic
interactions

Medium range
ion-ion and
ion-molecule
interactions

Short range
interactions

g_{LR}^E : Debye-Huckel model

g_{MR}^E : A function of composition and ionic strength

g_{SR}^E : UNIQUAC model

[1] P. Wang, A. Anderko, R. D. Young, Fluid Phase Equilibr., 203 (2002) 141 - 176.

[2] P. Wang, A. Anderko, R. D. Springer, R. D. Young, J. Mol. Liq. 125 (2006) 37 - 44.

[3] B. H. Morland et. al, Ind. Eng. Chem. Res. 58 (2019), 22924 - 22933.

Estimating Fugacity Coefficients

- ϕ_i^{vap} are calculated from equation of state like SRK or Peng-Robinson

$$\phi_i(T, P, x) = \exp\left(\left(\int_0^P \left(\frac{\partial N z}{\partial N_i}\right)_{T, P, x_{j \neq i}} - 1\right) \frac{dP}{P}\right) \quad \text{where, } z = \frac{PV}{NRT}$$

- For example, let the vapor phase be represented by van der Waals equation of state:

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \quad \text{where, } a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \quad b = \sum_i x_i b_i \quad \text{Mixing rules}$$

$$\Rightarrow z = \frac{v}{v - b} - \frac{a}{vRT} \quad \Rightarrow \ln \phi_i = \ln\left(\frac{v}{v - b}\right) + \frac{b_i}{v - b} - \frac{2\sqrt{a_i} \sum_j x_j \sqrt{a_j}}{vRT} - \ln z$$

Estimating Fugacity Coefficients

Mixed Solvent Electrolyte Model [1,2,3]

- ϕ_i^{vap} are calculated from the Soave – Redlich – Kwong (SRK) equation:

$$P = \frac{RT}{V - b} - \frac{a}{\sqrt{T}V(V + b)}$$

$$a_i = a(T_c, P_c) \text{ and } b_i = b(T_c, P_c)$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - k_{ij})$$

$$b = \sum_i x_i b_i$$

k_{ij}
↓
Fitting parameter
from expt. data.

[1] P. Wang, A. Anderko, R. D. Young, Fluid Phase Equilibr., 203 (2002) 141 - 176.

[2] P. Wang, A. Anderko, R. D. Springer, R. D. Young, J. Mol. Liq. 125 (2006) 37 – 44.

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Including Chemical Reactions

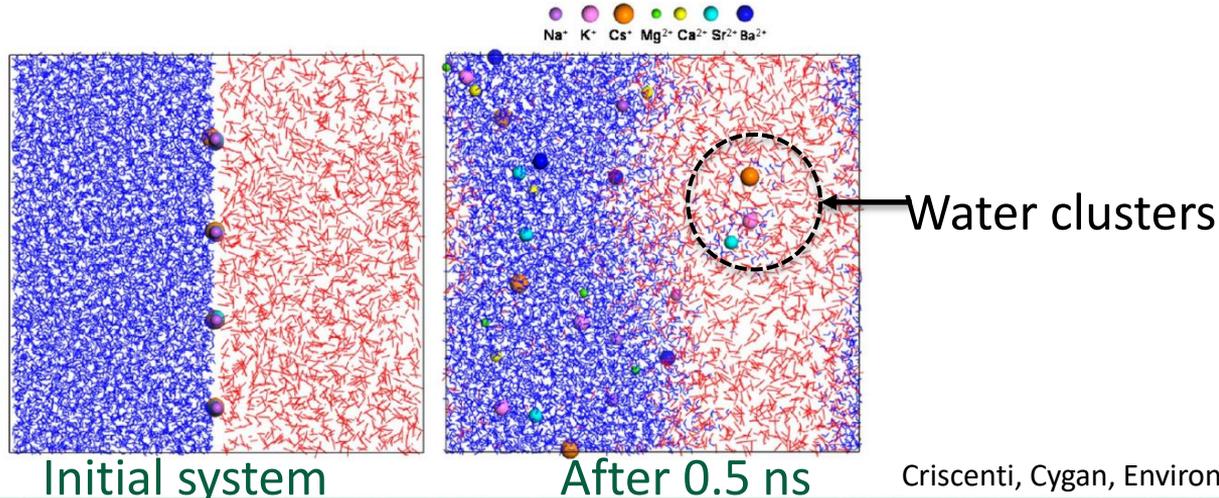
- Chemical reactions introduce constraints between chemical potential of species.

$$\sum_{i=1}^r \mu_i \nu_i^j = 0$$

ν_i^j represents stoichiometric coefficient of species i in the reaction j

Molecular Simulations

- Presence of impurities / metal surfaces alter conditions under which water / acid precipitates. Why? We can study this using molecular simulations.
- Study nucleation of water in dense phase CO₂ environment
 - a) Homogeneous nucleation
 - b) Nucleation in presence of impurities and/or metal surfaces



Criscenti, Cygan, Environmental Science and Technology, 2012

Key Takeaways

- A thermodynamic model to predict water/acid solubility in dense phase CO₂ with speciation will be build.
- With the help of molecular simulations, the fundamental mechanisms involved homogeneous and heterogeneous nucleation of water in different conditions will be determined.

Next Steps

- Once we have a working thermodynamic model, we will extend it to include other species like glycols and amines.
- We will combine thermodynamic modeling to corrosion to provide a mechanistic model to predict corrosion rates under different conditions.

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Including Chemical Reactions

- **Chemical reactions introduce constraints between chemical potential of species.**
- Consider a system of r species with q possible chemical reactions. Each chemical reaction is given by:

$$0 \Rightarrow \sum_{i=1}^r v_i^j B_i \quad \forall j \in [1, q]$$

B_i represents a species and v_i^j represents its stoichiometric coefficient in the reaction j

- For a reaction j , the extent of the reaction ε_j is given by, $dN_i = v_i^j d\varepsilon_j$, where N_i is the number of moles of the species B_i .

Including Chemical Reactions

- At constant temperature, T and pressure, P , the Gibbs free energy, G is minimized.

$$dG = \sum_{i=1}^r \mu_i dN_i$$

Now substituting $dN_i = \nu_i^j d\varepsilon_j$

$$\rightarrow dG = \sum_{j=1}^q \left(\sum_{i=1}^r \mu_i \nu_i^j \right) d\varepsilon_j$$

$$\left(\frac{\partial G}{\partial \varepsilon_j} \right)_{T,P,\{\varepsilon_{k \neq j}\}} = \sum_{i=1}^r \mu_i \nu_i^j = 0$$

This constraint can be written in terms of activity coefficients.