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Modeling the thermodynamic properties of CO₂ aqueous solution using a combination of HKF and Pitzer equations

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Abstract n°2017

1 Although the CO₂-H₂O geochemical system has been extensively studied, it is still difficult to find a model thermodynamically-consistent, able to explain with equivalent confidence the experimental data of density, heat capacity and reciprocal solubility in the conditions range of CO₂ sequestration.

2 Theoretical background
CO₂-H₂O system was modeled using a gamma-phi approach for the liquid-gas equilibrium

$$m_{CO_2} \gamma_{CO_2} K_{CO_2}^0 \exp\left(\frac{\bar{V}_{CO_2}(P - P^0)}{RT}\right) = y_{CO_2} \phi_{CO_2} P$$

$$a_{H_2O} K_{H_2O}^0 \exp\left(\frac{\bar{V}_{H_2O}(P - P^0)}{RT}\right) = y_{H_2O} \phi_{H_2O} P$$

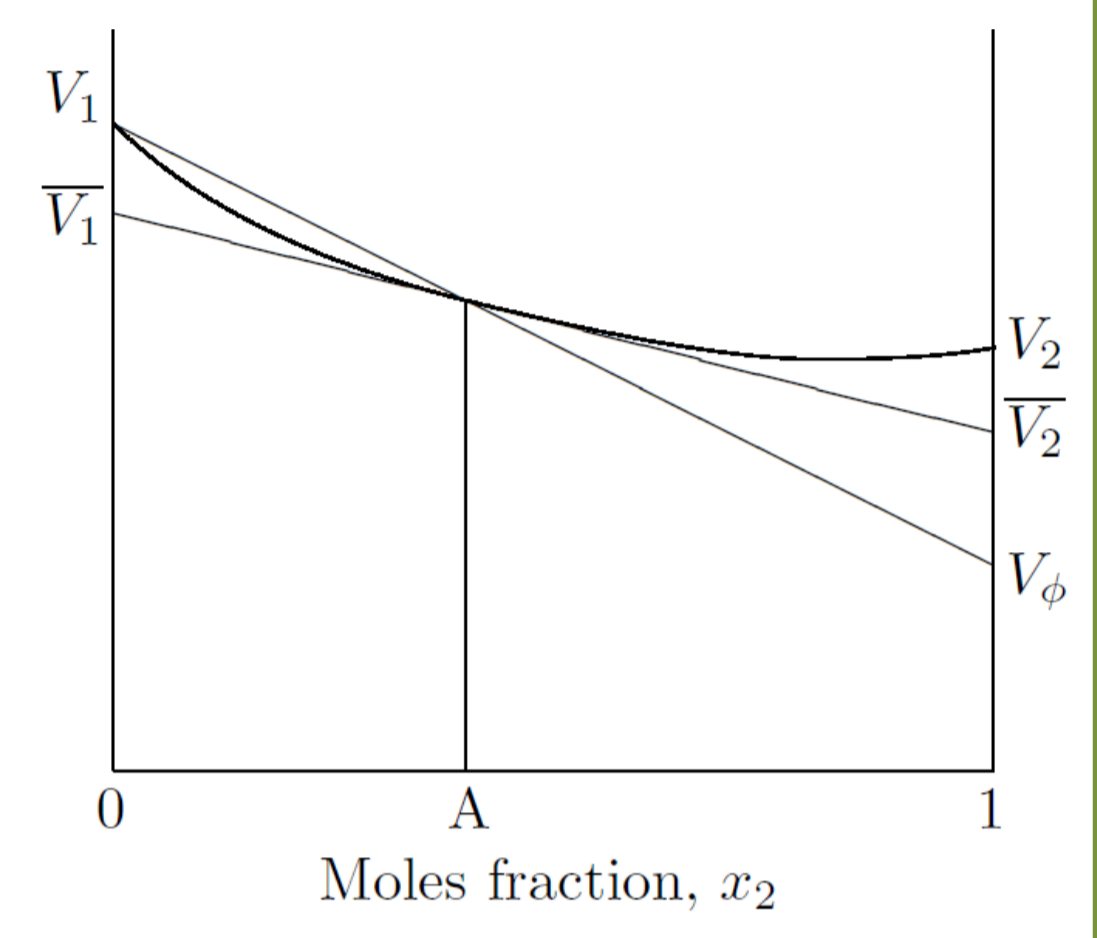
With
 γ : activity coefficient of aqueous CO₂ calculated with the Pitzer formalism
 ϕ : fugacity coefficient calculated with the Peng-Robinson equation of state
 K: equilibrium constant at water saturation P⁰
 V: partial molar volume average over P range
 In the aqueous phase, HKF [1] and Pitzer [2] equations are implemented in PhreeSCALE [3] that allows to calculate standard, partial and apparent properties.

$$\frac{G^{ex}}{w_w RT} = f(I) + \sum_i \sum_j \lambda_{ij} m_i m_j$$

$\frac{\partial G^{ex}}{\partial w_w} \rightarrow \Phi - 1 = \dots$
 $\frac{\partial G^{ex}}{\partial n_i} \rightarrow \gamma_i = \dots$
 $\frac{\partial^2 G^{ex}}{\partial T^2} \rightarrow C_{p,\Phi} = C_p^0 + \dots$
 $\frac{\partial G^{ex}}{\partial P} \rightarrow V_\Phi = V_0 + \dots$

3 Compilation of experimental data
TP range relevant for CO₂ sequestration: Hydrate < T < 200°C, 0 < P < 80MPa.

- Apparent molar volume V_φ [4-6] (density)
 - Apparent molar heat capacity Cp_φ [4,7]
 - Reciprocal solubility [large compilation]
- m_{CO2} in aqueous phase
 y_{H2O} in CO₂-rich phase



4 Methodology

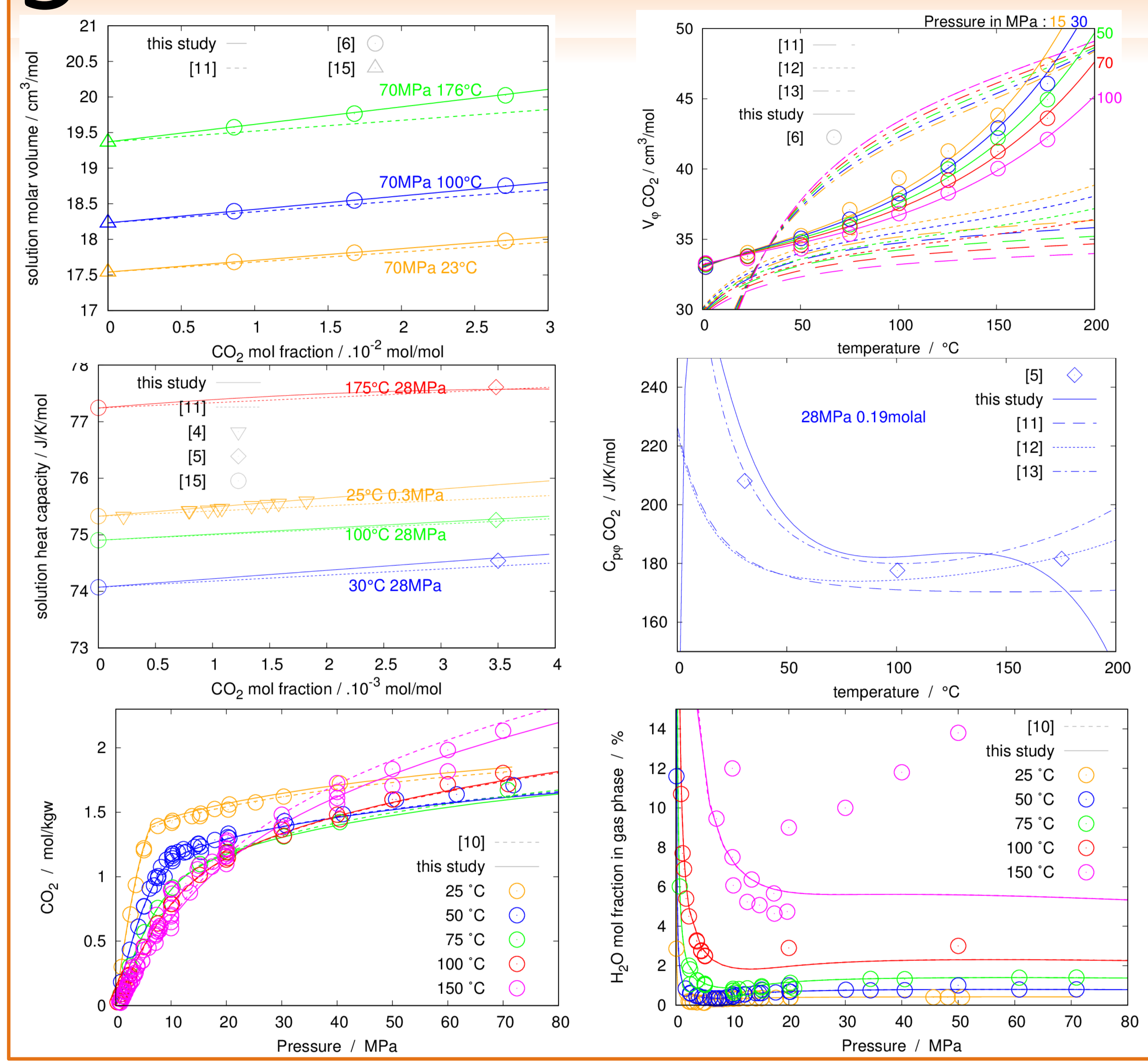
- Comparison of various sets of HKF parameters [11-13]
- $$V_{CO_2}^0 = a_1 + \frac{a_2}{\psi + P} + \left(\frac{1}{T - \theta}\right) \left(a_3 + \frac{a_4}{\psi + P}\right) - \omega Q$$
- $$Cp_{CO_2}^0 = c_1 + \frac{c_2}{(T - \theta)^2} - \left(\frac{2T}{(T - \theta)^3}\right) \left(a_3(P - Pr) + a_4 \ln\left(\frac{\psi + P}{\psi + Pr}\right)\right) + \omega TX$$

Species-specific parameters for HKF equations (units J.mol⁻¹[.K][.bar⁻¹])

	10.a ₁	10 ⁻² .a ₂	a ₃	10 ⁻⁴ .a ₄	c ₁	10 ⁻⁴ .c ₂	10 ⁻⁶ .ω
[11]	26.14	31.26	11.77	-12.92	167.50	36.82	-0.08
[12]	26.14	31.26	11.77	-12.92	160.89	22.40	-0.81
[13]	64	-42	-232	31	154	15	-1.31
This study	31.01	1.71	8.77	-5.12	60.28	61.04	-6.79

- Comparison with others formalisms when possible [9-10]
- New optimization of HKF parameters (with PEST® software) on the data compilation
- Test the use of a T-dependent λ_{CO2-CO2} interaction parameter.
 - γ_{CO2} become different to unity
 - Cp_φ become different to standard molar Cp

5 Preliminary results



6 Conclusions

No published set of HKF parameters was found to be able to correctly reproduce both Vm and Cp of aqueous CO₂. When using a T-dependent λ_{CO2-CO2}, the fit was improved. However further works are needed to avoid unrealistic extrapolation at higher temperatures.

[1] Tanger, 1988 ; [2] Pitzer, 1973 ; [3] Lach, 2016 ; [4] Barbero, 1983 ; [5] Hnedkovsky, 1996 ; [6] McBride, 2015 ; [7] Hnedkovski, 1997 ; [8] Sycher, 2003 ; [9] Appelo, 2013 ; [10] Appelo, 2014 ; [11] Shock, 1989 ; [12] Shulte, 2001 ; [13] Plyasunov, 2001 ; [14] Drummond, 1981 ; [15] IAPWS-97