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Abstract n°2017

Modeling the thermodynamic properties of CO_2 aqueous solution using a combination of HKF and Pitzer equations

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Geoscience for a sustainable Earth brgm

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Although the CO_2-H_2O 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 CO_2 sequestration.

2 Theoretical background

CO_2-H_2O system was modeled using a gamma-phi approach for the liquid-gas equilibrium

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

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

With

ϒ : activity coefficient of aqueous CO_2 calculated with the Pitzer formalism

ψ: fugacity coefficient calculated with the Peng-Robinson equation of state

K: equilibrium constant at water saturation P^0

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.

$$\frac{G^{ex}}{w_wRT}=f(I)+\sum_i\sum_j\lambda_{ij}m_im_j$$

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

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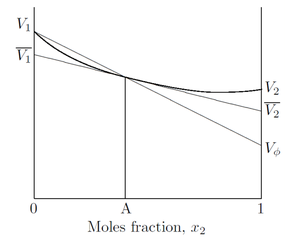
3 Compilation of experimental data

TP range relevant for CO_2 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 CO_2-rich phase



4 Methodology

- Comparison of various sets of HKF parameters [11-13]

$$V^0_{CO_2}=a_1+\frac{a_2}{\Psi+P}+\left(\frac{1}{T-\Theta}\right)\left(a_3+\frac{a_4}{\Psi+P}\right)-\omega Q$$

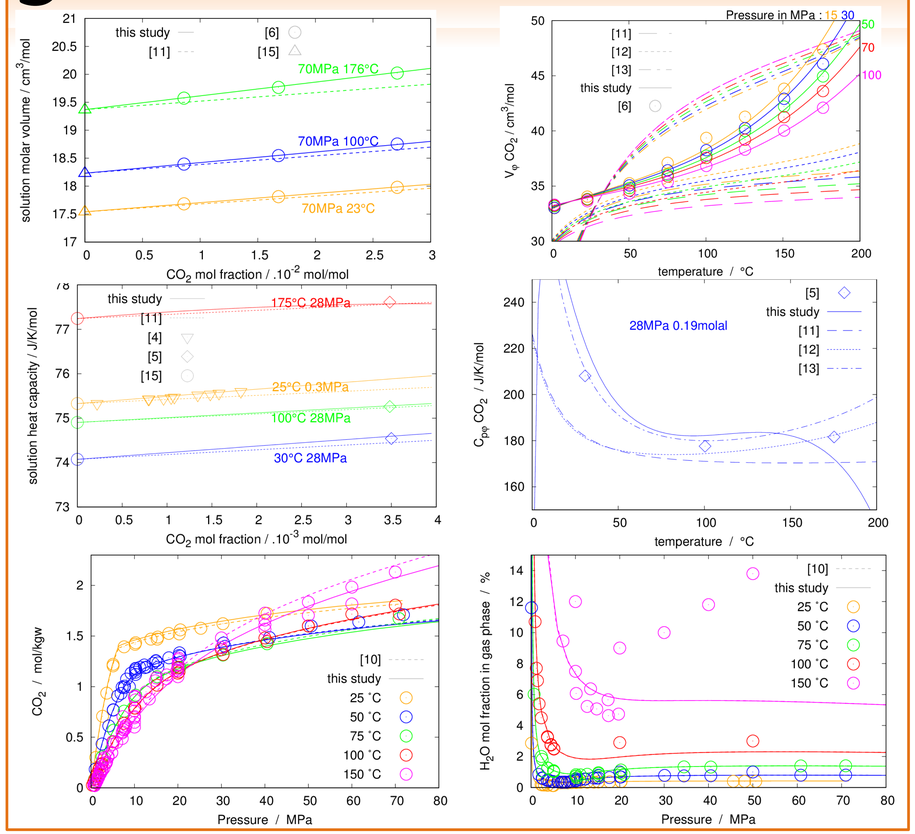
$$Cp^0_{CO_2}=c_1+\frac{c_2}{(T-\Theta)^2}-\left(\frac{2T}{(T-\Theta)^3}\right)\left(a_3(P-Pr)+a_4\ln\left(\frac{\Psi+P}{\Psi+Pr}\right)\right)+\omega TX$$

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	$10^{-4}.c_2$	$10^{-6}.\omega$
[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 $\lambda_{CO2\text{-}CO2}$ 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 CO_2. When using a T-dependent $\lambda_{CO2\text{-}CO2}$, 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] Spycher, 2003 ; [9] Appelo, 2013; [10] Appelo, 2014 ; [11] Shock, 1989 ; [12] Shulte, 2001 ; [13] Plyasunov, 2001 ; [14] Drummond, 1981 ; [15] IAPWS-97