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

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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.

1 Theoretical background

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

\[ m_{CO2}Y_{CO2}K_{CO2}^{0}e^{\left(\frac{PO\left(P-P^0\right)}{RT}\right)} = y_{CO2}\varphi_{CO2}P \]

\[ a_{H2O}K_{H2O}^{0}e^{\left(\frac{P_{H2O}\left(P-P^0\right)}{RT}\right)} = y_{H2O}\varphi_{H2O}P \]

With

\( T\): activity coefficient of aqueous CO₂ calculated with the Pitzer formalism

\( \psi\): fugacity coefficient calculated with the Peng-Robinson equation of state

\( K\): equilibrium constant at water saturation \( P^0\)


2 Compilation of experimental data

TP range relevant for CO₂ sequestration:

Hydrate<T<200°C, 0<P<80MPa.

- Apparent molar volume \( V_{\phi} \) [4-6] (density)
- Apparent molar heat capacity \( C_{p\phi} \) [4,7]
- Reciprocal solubility [large compilation]

\( m_{CO2} \) in aqueous phase

\( Y_{H2O} \) in CO₂-rich phase

3 Methodology

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

\[ V_{CO2}^0 = a_1 + \frac{a_2}{\psi + P} + \left( \frac{1}{T-\theta} \right) \left( a_3 + \frac{a_4}{\psi + P} \right) - \omega Q \]

\[ C_{pCO2}^0 = c_1 + \frac{c_2}{T-\theta} - \left( \frac{2T}{T-\theta} \right)^2 \left( a_3(P-P^r) + a_4\ln\left(\psi + P + P^r\right) \right) + \psi TX \]

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

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<th>10⁻⁶a₁</th>
<th>10⁻²a₂</th>
<th>a₃</th>
<th>10⁻⁴a₄</th>
<th>c₁</th>
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</table>

- Comparison with other formalisms when possible [9-10]
- New optimization of HKF parameters (with PEST® software) on the data compilation
- Test the use of a T-dependent \( \lambda_{CO2-CO2} \) interaction parameter.
  - \( Y_{CO2} \) become different to unity
  - \( C_{p\phi} \) become different to standard molar \( C_p \)

4 Conclusions

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