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Modeling the thermodynamic properties of CO₂ aqueous solution using a combination of HKF and Pitzer equations
Parmentier M.⁽¹⁾, Lach A.⁽²⁾, Andre L.⁽²⁾, Lassin A.⁽²⁾

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. Comparison with others formalisms
Pitzer 1981 P = \frac{P_C}{\psi_C} ϒ

HKF λ CO

2. Theoretical background
CO₂-H₂O system was modeled using a gamma-phi approach for the liquid-gas equilibrium
\begin{align*}
m_{CO2}Y_{CO2}K_{CO2}e^{\left(\frac{V_{CO2}(P - P^0)}{RT}\right)} &= y_{CO2}\varphi_{CO2}P \\
a_{H2O}Y_{H2O}K_{H2O}e^{\left(\frac{V_{H2O}(P - P^0)}{RT}\right)} &= y_{H2O}\varphi_{H2O}P
\end{align*}

With
\begin{align*}
T : & \text{ activity coefficient of aqueous CO}_2 \text{ calculated with the Pitzer formalism} \\
ψ : & \text{ fugacity coefficient calculated with the Peng-Robinson equation of state} \\
K : & \text{ equilibrium constant at water saturation P}^0 \\
\end{align*}

3. Compilation of experimental data
TP range relevant for CO₂ sequestration: Hydrate<T<200°C, 0<P<800MPa.
- Apparent molar volume V₀ [4-6] (density )
- Apparent molar heat capacity Cₚ [4,7]
- Reciprocal solubility [large compilation]
m_{CO2} in aqueous phase

4. Methodology
- Comparison of various sets of HKF parameters [11-13]

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.

\begin{align*}
\frac{C^{ex}}{wPRT} &= f(l) + \sum_j \lambda_j m_j m_j \\
-\varphi &= 1 + \frac{\partial C^{ex}}{\partial w} \frac{\partial C^{ex}}{\partial T} \frac{\partial C^{ex}}{\partial P} \frac{\varphi}{\partial P} \\
V₀ &= \varphi₀ + \ldots
\end{align*}

\begin{align*}
V^{0}_{CO2} &= a_1 + a_2 \frac{\psi}{\psi + P} + \left(\frac{1}{T - \theta}\right) (a_3 + a_4 \frac{\psi}{\psi + P}) - \omega Q \\
C^{P}_{CO2} &= c_1 + c_2 \frac{T}{(T - \theta)^2} \left(\frac{2T}{(T - \theta)^2}\right) (a_3 (P - Pr) + a_4 \ln\left[\frac{\psi + P}{\psi + P - Pr}\right]) + \omega TX \\
\text{Species-specific parameters for HKF equations (units j.mol⁻¹.K⁻¹.bar⁻¹)}
\end{align*}

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<th>a₀, a₁, a₂, c₁, c₂, c₄, c₅, c₆, c₇, c₈</th>
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<tr>
<td>10.14, 31.16, 17.77, -12.92, 167.50</td>
<td>36.82, -0.08</td>
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<td>31.01, 1.71, 8.77, -5.12, 60.28, 61.04, -6.79</td>
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