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

Marc Parmentier, Adeline Lach, Laurent André, Arnault Lassin

To cite this version:
Marc Parmentier, Adeline Lach, Laurent André, Arnault Lassin. Modeling the thermodynamic properties of CO2 aqueous solution using a combination of HKF and Pitzer equations. 43rd IAH Congress, Sep 2016, Montpellier, France. hal-02457858

HAL Id: hal-02457858
https://hal-brgm.archives-ouvertes.fr/hal-02457858
Submitted on 28 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
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.

Theoretical background

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

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

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

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 \( P^0 \) 

\[ \frac{C_{ex}}{w_{ex}RT} = f(\theta) + \sum \lambda_i m_i m_j \]

\[ \frac{\partial \varphi_{ex}}{\partial w_{ex}} = \theta \frac{\partial \varphi_{ex}}{\partial \theta} + \sum \lambda_i m_i m_j \]

\( \Phi = 1 - \ldots \)

\[ \varphi_{ex} \]

\[ V_{ex} = V_{0} + \ldots \]

Compilation of experimental data

TP range relevant for CO₂ sequestration: Hydrate<T<200°C, 0<P<800MPa.

- Apparent molar volume \( V_\psi \) [4-6] (density )
- Apparent molar heat capacity \( C_p_\psi \) [4,7]
- Reciprocal solubility [large compilation]

\( m_{CO₂} \) in aqueous phase

\( V_{H₂O} \) in CO₂-rich phase

Methodology

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

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

\[ C_p_{CO₂} = c_1 + \frac{c_2}{(T - \theta)^2} - \left( \frac{2T}{T - \theta} \right)^{\frac{1}{2}} \left( a_3(P - Pr) + a_4 \ln \left( \frac{\psi + P - Pr}{\psi + P} \right) + \omega \xi \right) \]

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

<table>
<thead>
<tr>
<th>( a_{1} )</th>
<th>( a_{2} )</th>
<th>( a_{3} )</th>
<th>( a_{4} )</th>
<th>( c_{1} )</th>
<th>( c_{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[11]</td>
<td>26.14</td>
<td>31.26</td>
<td>11.77</td>
<td>-12.92</td>
<td>167.50</td>
</tr>
<tr>
<td>[12]</td>
<td>26.14</td>
<td>31.26</td>
<td>11.77</td>
<td>-12.92</td>
<td>168.9</td>
</tr>
</tbody>
</table>

This study

31.01 | 1.71 | 8.77 | -5.12 | 60.28 | 61.04 | -6.79 |

- 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.
  - \( \gamma_{CO₂} \) become different to unity
  - \( C_p_\psi \) become different to standard molar \( C_p \)

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.