Implementation of a Gibbs energy explicit seawater equation in Helmholtz mixture models to represent the interaction of brines with CCS-relevant fluids

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Motivation

- Properties of CO_2-rich streams are calculated using accurate Helmholtz-energy models for pipeline and ship transport
- For scenarios involving brines, properties are usually calculated using simpler equations of state in conjunction with Gibbs-enthalpy based brine models
  - Inconsistencies between property calculations in transport and storage
  - Difficulties in closing mass and energy balances
  - Difficulties in an optimization of the whole CCS chain

- Goal of this project: Combine Helmholtz models for CO_2-rich mixtures and Gibbs-enthalpy based brine models to allow for consistent calculations

Helmholtz Equations of State

- Fundamental Equation of State (EOS)
  - Reduced density $\delta = \rho/\rho_\mathrm{r}$ and inverse reduced temperature $\tau = T_\mathrm{r}/T$
  - Ideal part $\alpha^\mathrm{o}(\rho, T)$
  - Residual part $\alpha^\mathrm{r}(\tau, \delta)$

- Multi fluid approach with corresponding state and optional departure function by Lemmon and Tillner-Roth

$$\alpha(\delta, \tau, \bar{x}) = \boxed{\sum_{i=1}^{N} x_i \left[\boxed{\alpha_{\mathrm{o}i}^{\mathrm{o}}(\rho, T)} + \ln x_i\right]} + \boxed{\sum_{i=1}^{N} x_i \boxed{\alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta, \tau)}} + \boxed{\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha_{ij}^{\mathrm{r}}(\delta, \tau)}$$

IAPWS Seawater model

- Fundamental EOS explicit in specific Gibbs energy $g(S_\mathrm{A},T,p)$
- Absolute Salinity S_A describes mass salt per mass seawater
- Saline contribution is added to pure water (IAPWS-95)

$$g(S,T,p) = \boxed{g^{\mathrm{W}}(T,p)} + \boxed{g^{S}(S_\mathrm{A},T,p)}$$

$$g^{\mathrm{W}}\big(T,\rho(p)\big) = RT(1+\alpha^{\mathrm{o}}+\alpha^{\mathrm{r}}+\delta\alpha^{\mathrm{r}}_{\delta})$$

- Calculated with IAPWS-95
- Density iterations necessary

$$p(T,\rho) = [1+\delta a^{\mathrm{r}}(\tau,\delta)]\,\rho RT$$

$$g^{S}(S_A,T,p) = g^{*}\sum_{k=0}^{5}\sum_{j=0}^{6}\left(g_{1jk}\,\xi^{2}\ln\xi + \sum_{i=2}^{7} g_{ijk}\,\xi^{2}\right)\tau_{\mathrm{s}}^{j}\,\pi^{k}$$

ξ: reduced Salinity
τ_S : reduced temperature
π : reduced pressure
g^* : 1 J/kg and g_{ijk}: Equation parameters

Combination of the EOS

- Both EOS are fundamental equations of state
- Main potential and variables can be transferred via Legendre transformation
- Equal properties allows for the determination of equal derivatives

$$p(T, \rho) = [1 + \delta\alpha_{\delta}^{\mathrm{r}}]\, \rho R T$$

$$\delta\alpha_{\delta}^{\mathrm{r}} = \frac{p}{\rho R T} - 1$$

$$\frac{1}{\rho} = \frac{\partial g}{\partial p} = g_p$$

$$\delta\alpha_{\delta}^{\mathrm{r}} = \frac{p g_p}{R T} - 1$$

Implementation of the combined model

- Seawater model based on IAPWS-95 → integration in Helmholtz mixture models possible

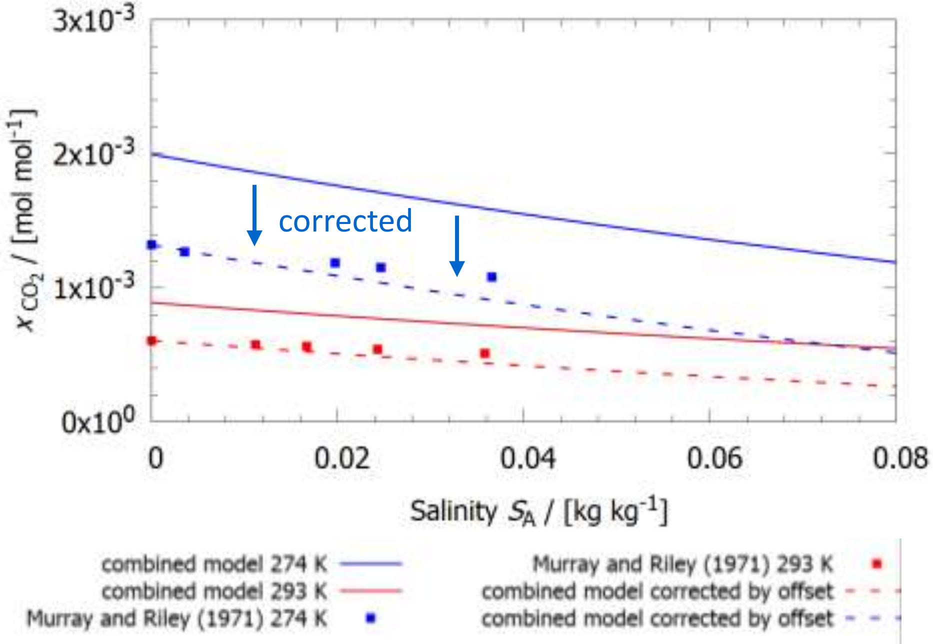
$$\alpha_{\mathrm{Helm}} = x_{\mathrm{W}}\,\boxed{\alpha^{\mathrm{o}}_{\mathrm{W}}(T,\rho)} + x_{\mathrm{CO_2}}\,\alpha^{\mathrm{o}}_{\mathrm{CO_2}}(T,\rho) + x_{\mathrm{W}} \ln x_{\mathrm{W}} + x_{\mathrm{CO_2}} \ln x_{\mathrm{CO_2}}$$
$$+ x_{\mathrm{W}}\,\boxed{\alpha^{\mathrm{r}}_{\mathrm{W}}(\tau,\delta)} + x_{\mathrm{CO_2}}\,\alpha^{\mathrm{r}}_{\mathrm{CO_2}}(\tau,\delta) + \Delta\alpha^{\mathrm{r}}_{\mathrm{Dep}}$$

$$\alpha_{\mathrm{seaw}} = \alpha^{\mathrm{o}}_{\mathrm{W}}(T,\rho) + \alpha^{\mathrm{r}}_{\mathrm{W}}(\tau,\delta) + \alpha_{\mathrm{saline}}(T,p,S_A)$$

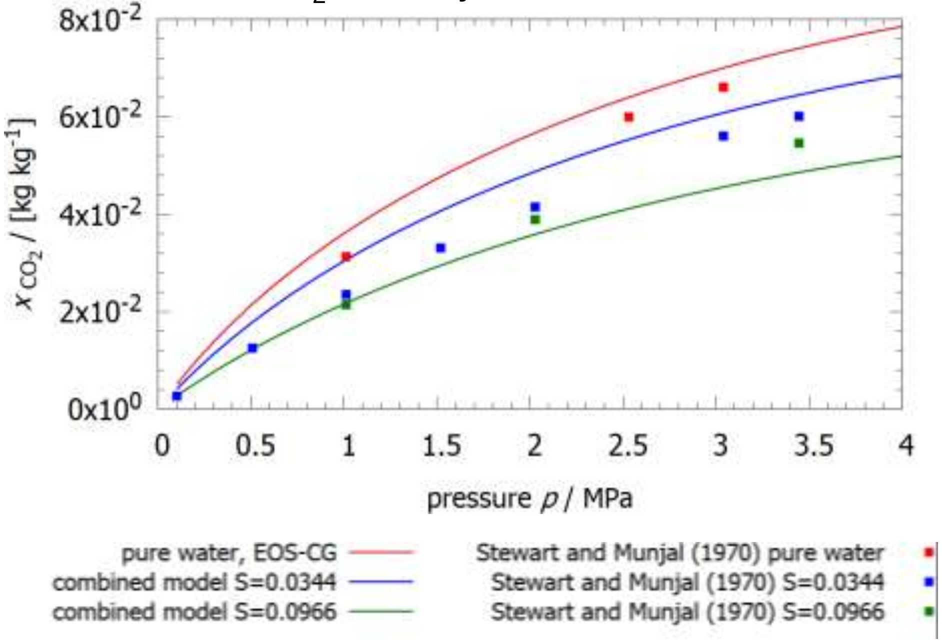
$$\alpha_{\mathrm{Helm+seaw}} = x_{\mathrm{seaw}}\,\alpha_{\mathrm{seaw}} + x_{\mathrm{CO_2}}\alpha^{\mathrm{o}}_{\mathrm{CO_2}}(T,\rho) + x_{\mathrm{seaw}} \ln x_{\mathrm{seaw}} + x_{\mathrm{CO_2}} \ln x_{\mathrm{CO_2}}$$
$$+ x_{\mathrm{CO_2}}\alpha^{\mathrm{r}}_{\mathrm{CO_2}}(\tau,\delta) + \Delta\alpha^{\mathrm{r}}_{\mathrm{Dep}}$$

Results – gas solubilities in seawater

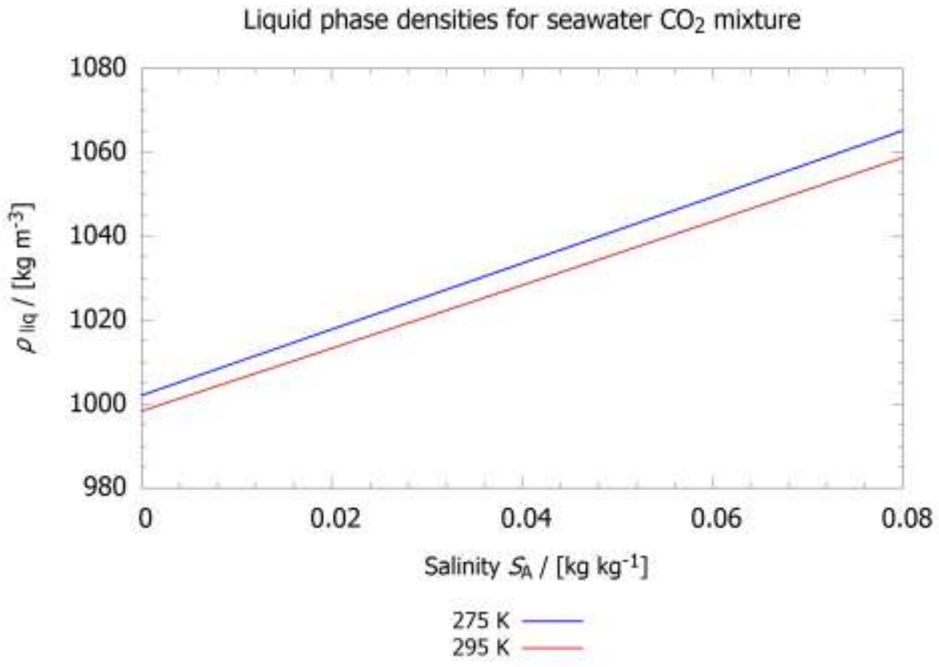
CO_2 solubility at atmospheric pressure

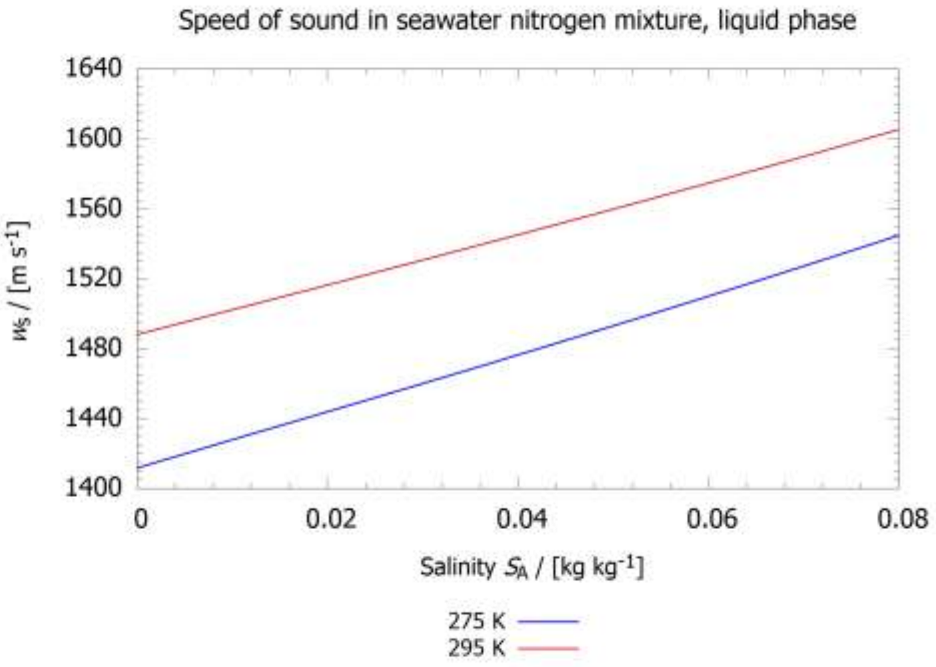


CO_2 solubility T = 273.15 K



Results for thermodynamic properties


Liquid phase densities for seawater CO_2 mixture


Speed of sound in seawater nitrogen mixture, liquid phase

Conclusion and Outlook

- Successful combination of the Gibbs and Helmholtz energy models for mixtures
- Caloric properties in the storage section can be calculated consistently with transport part
- Offset of gas solubilities in water at low pressures and ambient temperature mainly results from the basic Helmholtz energy model
- Further investigations for low solubility data is ongoing
- Model for larger range of validity with regards to salinities and pressures including adjusted mixture-specific parameters is needed

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