Towards an Accurate and Consistent Description of Thermodynamic Properties of Mixtures of CO_2 with Brines

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WEBINAR 3: HYDROGEN SUPPLY AND CO_2 INJECTION AND STORAGE

THERMODYNAMIK
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Empirical Helmholtz Energy Based Mixture Models

- Mixtures are described based on the 1990's approach by Lemmon & Tillner-Roth
  - Pure fluid equations of state
  - Mixing rules for δ_m und τ_m with up to 4 adjustable parameters
  - "Departure function" for an improved description of well measured mixtures

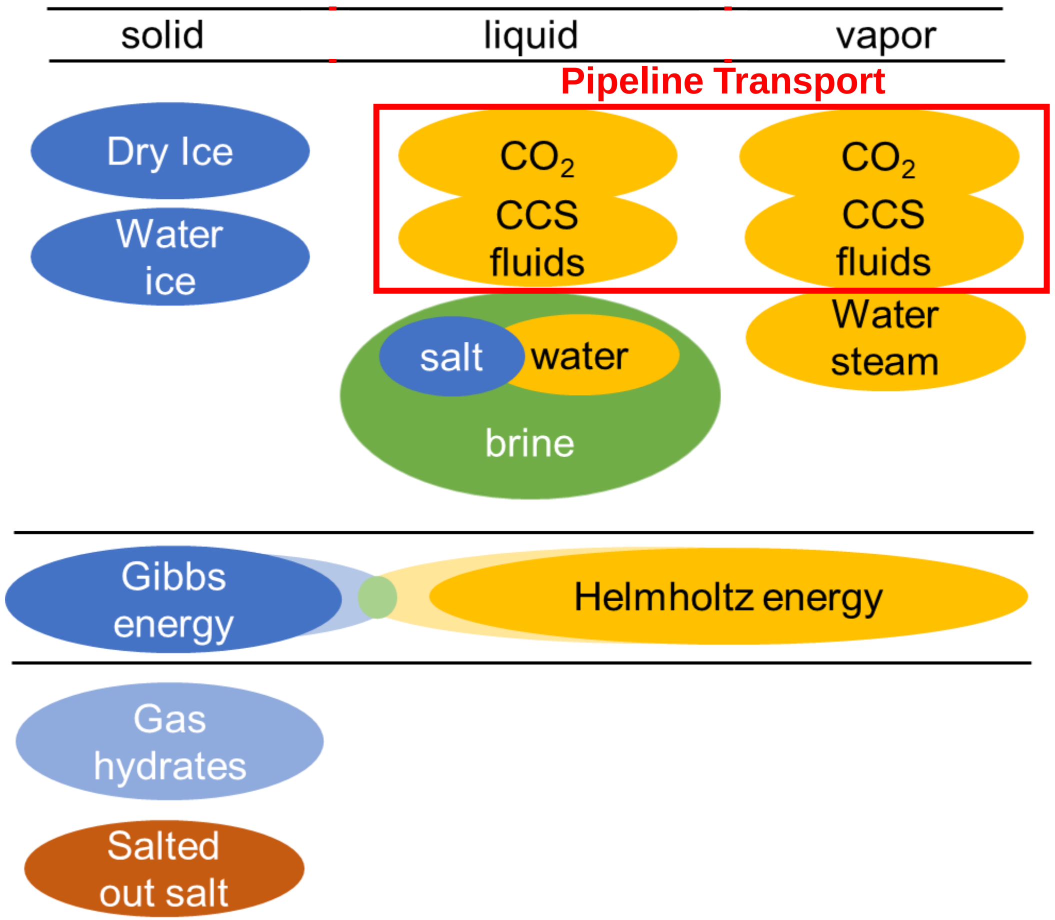
$$\alpha(\delta,\tau,\bar{x}) = \sum_{i=1}^{N} x_i\left[\alpha_{oi}^{0}(\rho,T)+\ln x_i\right]+\sum_{i=1}^{N} x_i\alpha_{oi}^{\mathrm{r}}(\delta_{\mathrm{m}},\tau_{\mathrm{m}}) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij}\alpha_{ij}^{\mathrm{r}}(\delta_{\mathrm{m}},\tau_{\mathrm{m}})$$

corresponding states with four parameters

departure function

- **In multicomponent mixtures models for all binary subsystems required**
- **Four Levels of accuracy:** (a) purely predictive description with combination rules, (b) fitting of the four corresponding states parameters, (c) generalized departure function, (d) binary specific departure function

Phases to be Considered in ELEGANCY



- Different phases are formulated in different types of fundamental equations
- Link between these property models is important for consistent models and calculations

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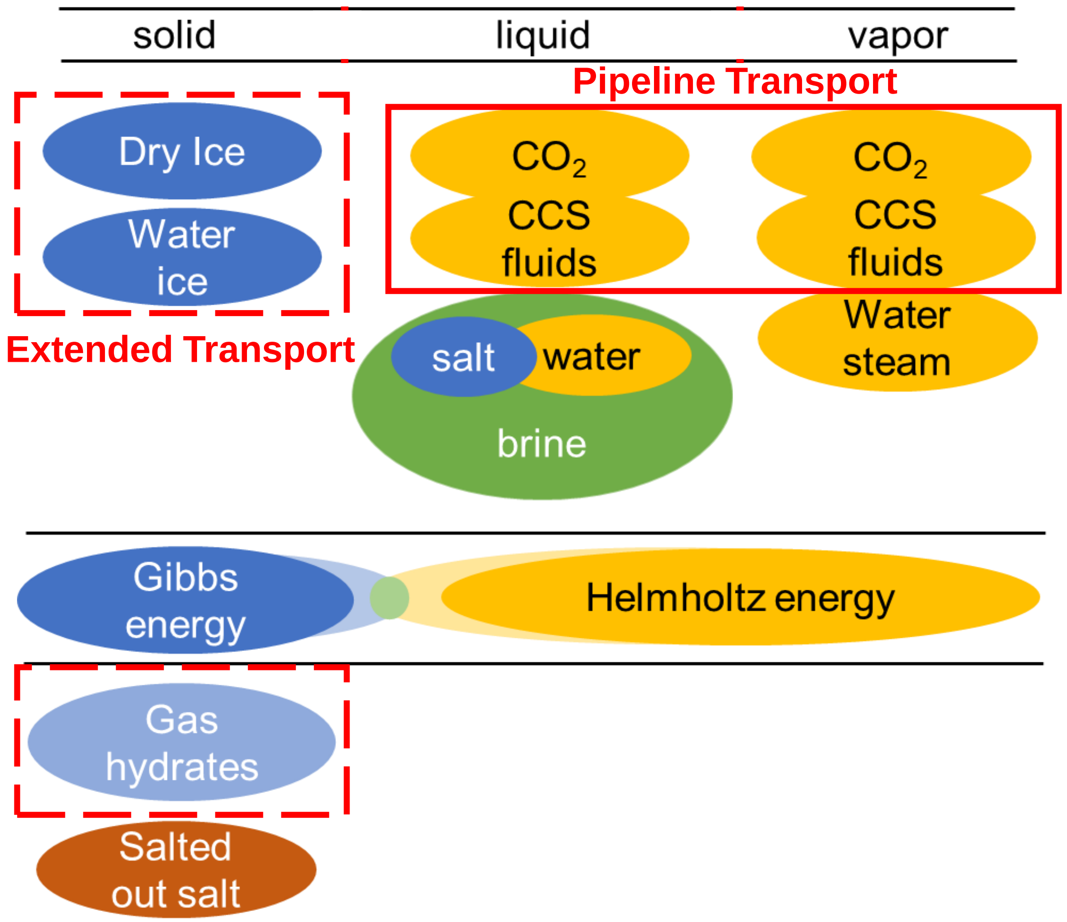

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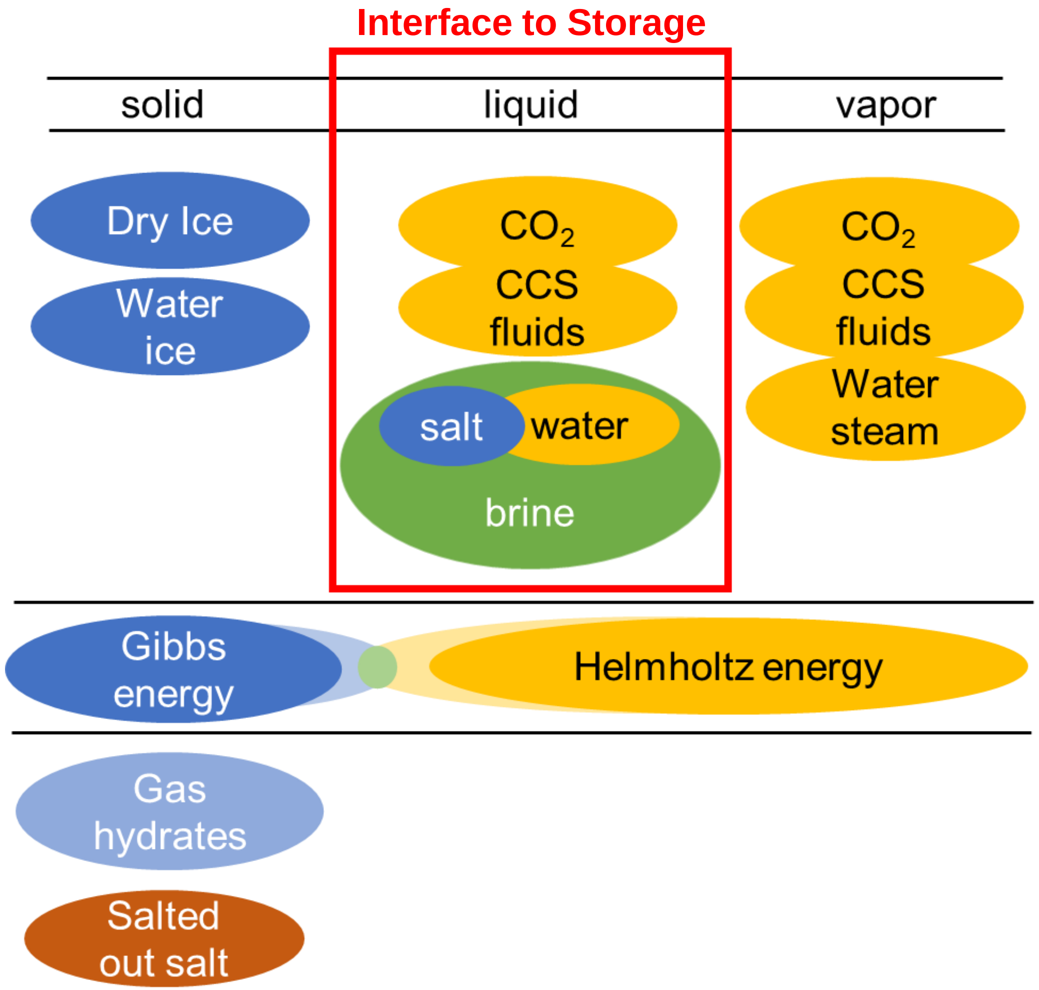

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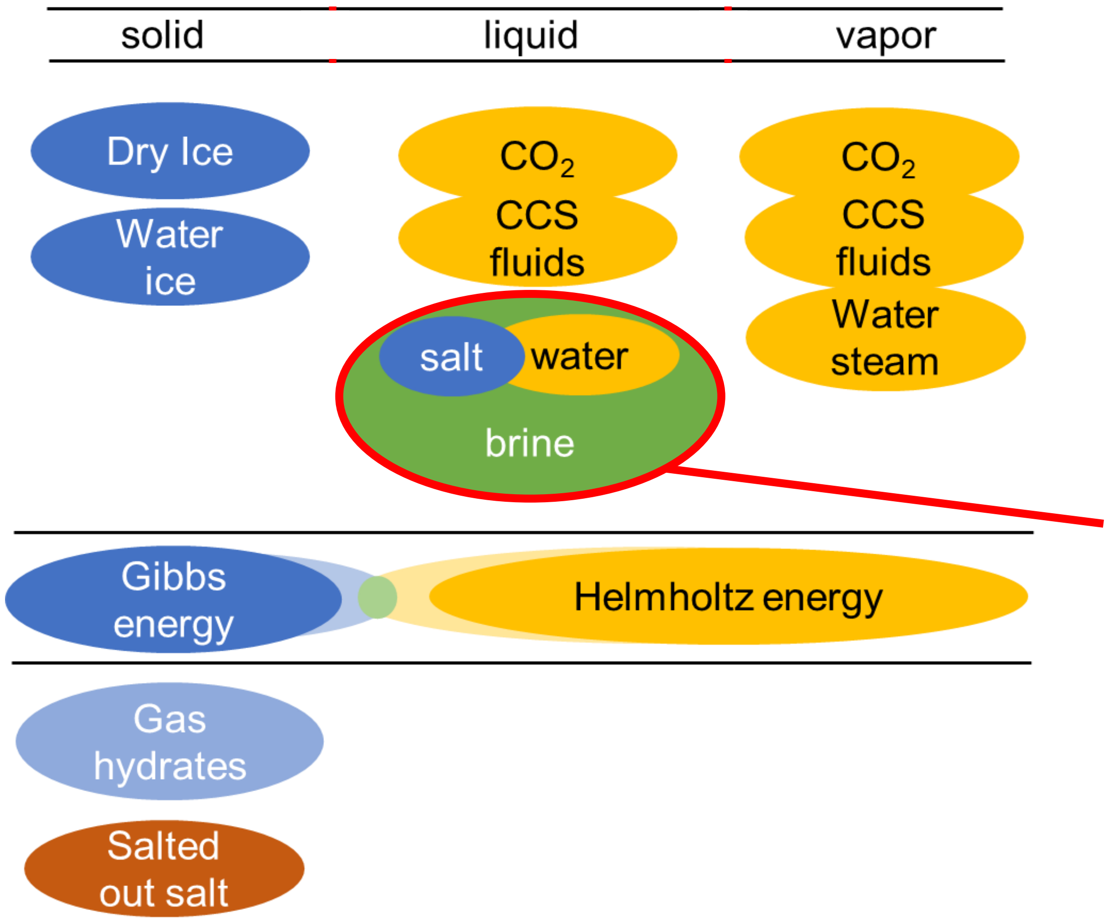

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1st approach / feasibility check: use the Gibbs energy based seawater equation of state by IAPWS to describe saltwater as liquid phase (IAPWS / IAPSO standard IAPWS R13-08 from 2008)

Combining EOS in Helmholtz and Gibbs Energy

- Both EOS are fundamental equations of state but are formulated in different potentials that have different independent variables
- Helmholtz and Gibbs energy and their independent variables can be transferred via Legendre transformation
- Equality of properties allows for the determination of equivalent derivatives

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

$$\delta\alpha^{\mathrm{r}}_{\delta} = \frac{p}{\rho RT} - 1$$

$$\frac{1}{\rho} = \frac{\partial g(T,p)}{\partial p} = g_p$$

$$\delta\alpha^{\mathrm{r}}_{\delta} = \frac{p g_p}{RT} - 1$$

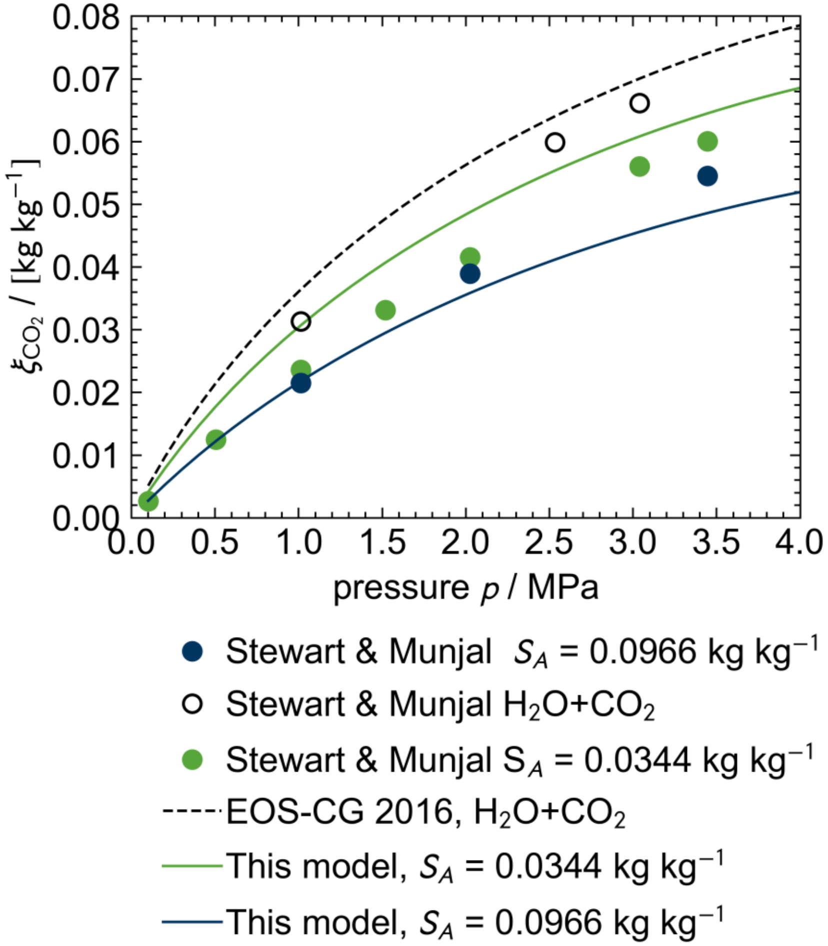
$$\delta = \rho/\rho_{\mathrm{c}}$$

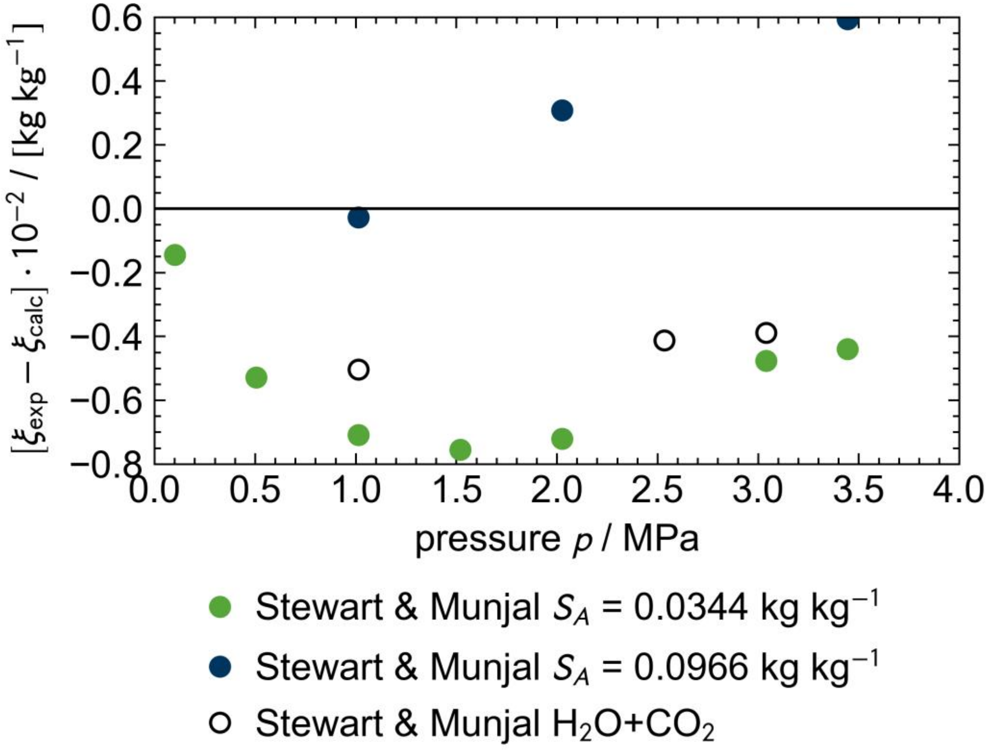
$$\alpha = a(T,\rho)/(RT) = \alpha^{\mathrm{o}} + \alpha^{\mathrm{r}}$$

$$\alpha^{\mathrm{r}}_{\delta} = (\partial\alpha^{r}/\partial\delta)_{\tau}$$

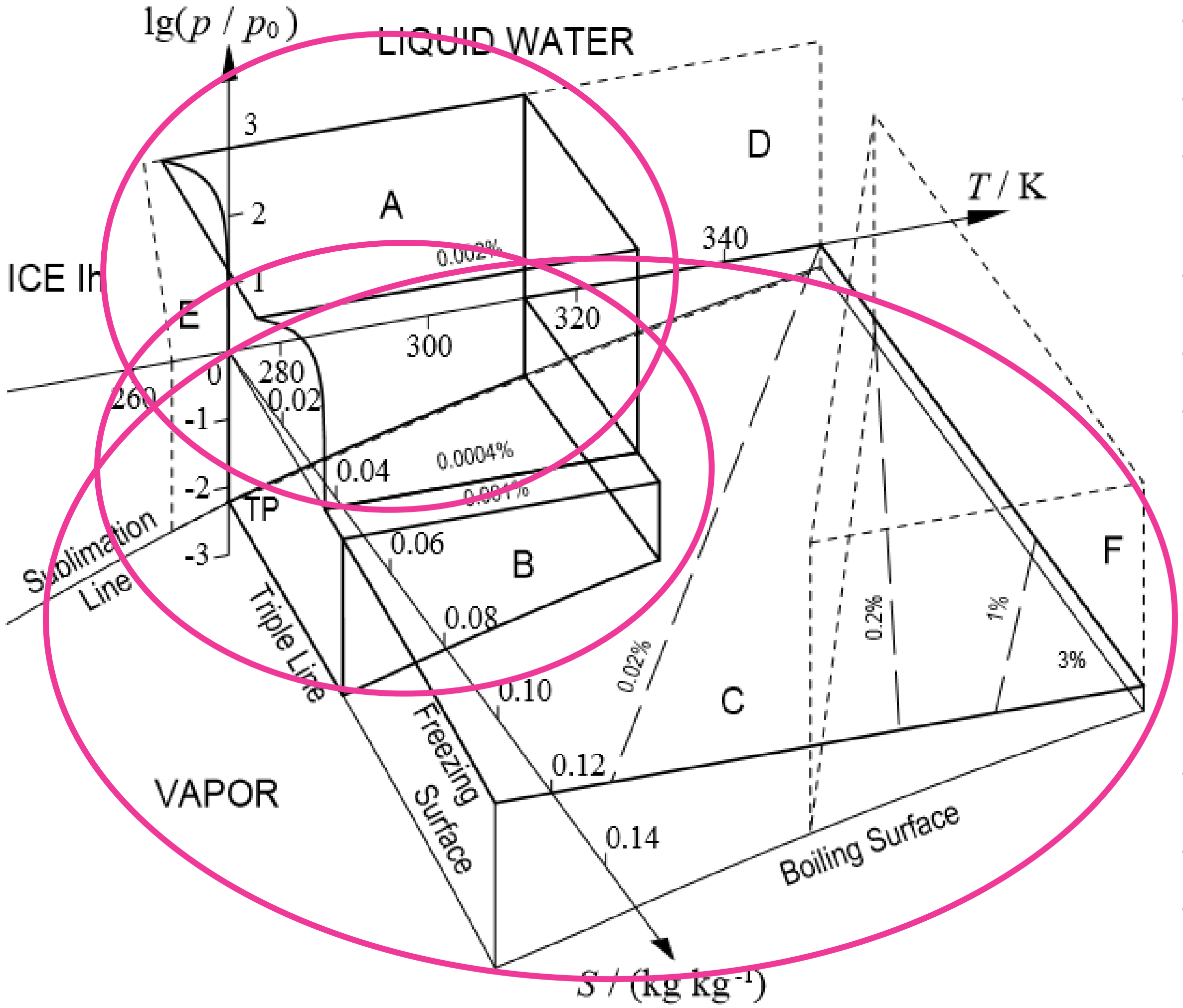
$$g_p = (\partial g/\partial p)_T$$

Test Case: Solubility Data for CO_2 in Seawater





Range of Validity and Limitations



Taken from: IAPWS, Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater, 2008

- $0 \leq S_A \leq 0.12 \frac{kg}{kg}$
- $261\ K \leq T \leq 353\ K$
- $0 < p \leq 10^8\ Pa$

Overall area, limitations below

- $0 \leq S_A \leq 0.042 \frac{kg}{kg}$
- $T_F \leq T \leq 313\ K$
- $101325\ Pa < p \leq 10^8\ Pa$

„Neptunian range“ (A)

- $0 \leq S_A \leq 0.05 \frac{kg}{kg}$
- $T_F \leq T \leq 313\ K$
- $p_{vap} < p \leq 101325\ Pa$

„low-pressure range“ (B)

- $0 \leq S_A \leq 0.12 \frac{kg}{kg}$
- $T_F \leq T \leq 353\ K$
- $p = 101325\ Pa$

Extension to high salinities and high temperatures at ambient pressure (C)

“normal salinity” $S_n = 0.03516504$ kg/kg

Implementation of the Brine Model by Pitzer

$$G(T,p,m) = m_{\mathrm{w}} G_{\mathrm{w}}(T,p) + n_{\mathrm{Salt}} G_{\mathrm{Salt}}(T,p) + G^{\mathrm{EX}}(T,p,m) + n_{\mathrm{salt}} \nu RT(\ln m - 1)$$

Gibbs Energy from IAPWS-95 (Helmholtz)

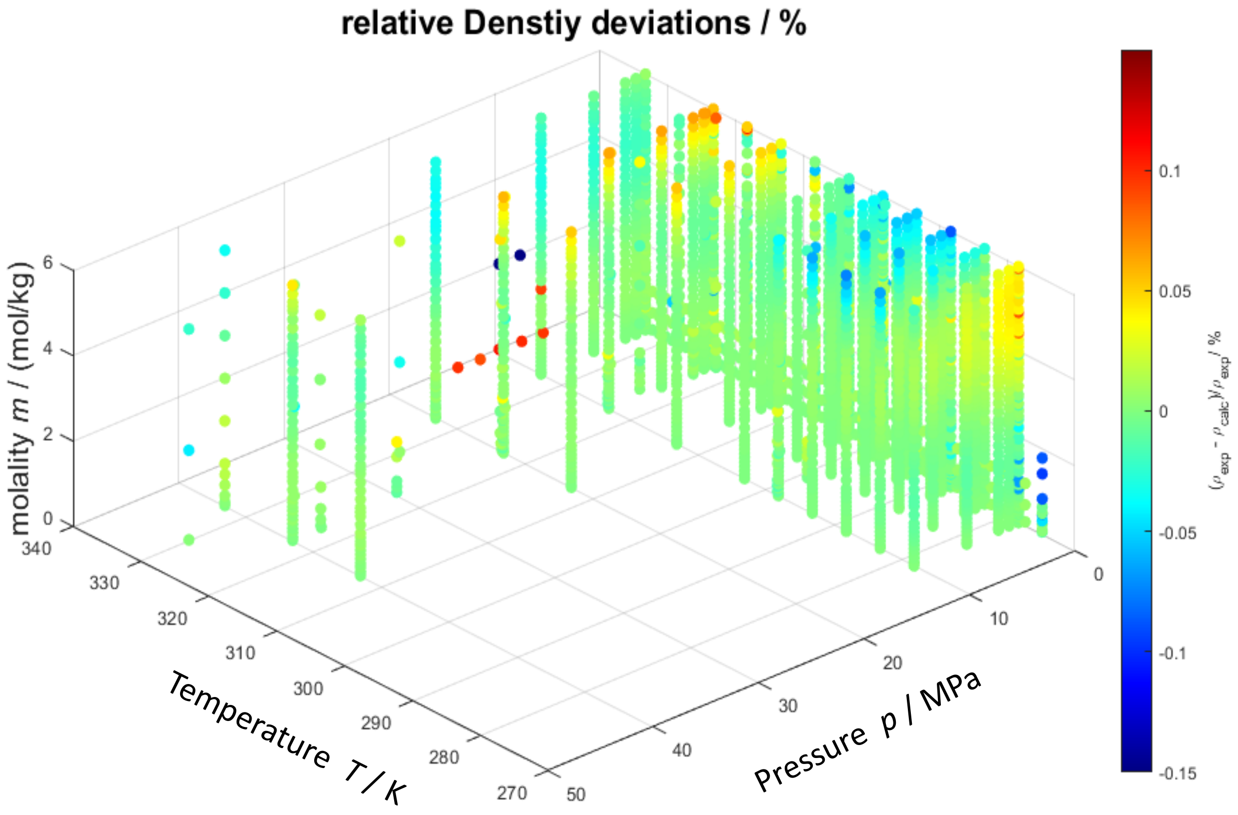
Gibbs energy of salt at infinite solution; contains adjustable parameters

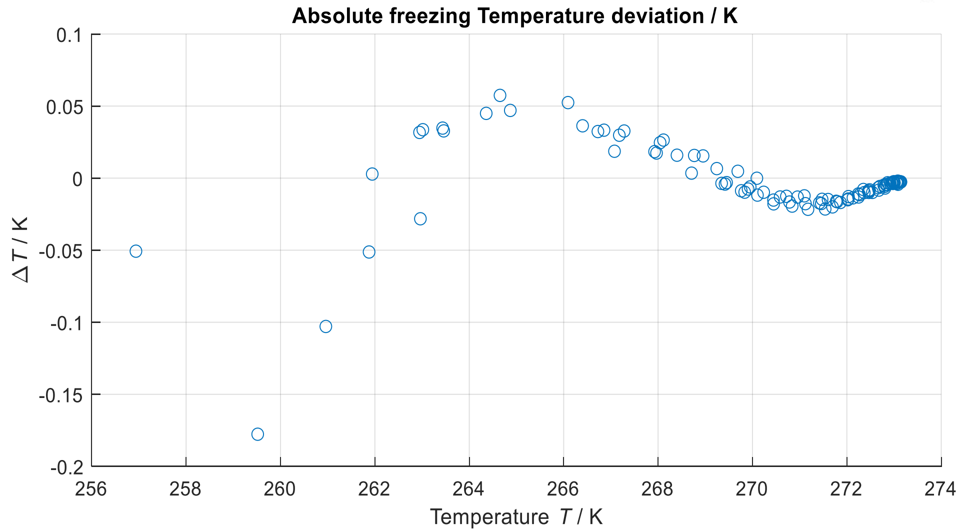
$$\frac{G^{\mathrm{EX}}}{m_w RT} = -A_{\Phi}\, h(I) + 2\nu_M \nu_X [m^2 B_{MX} + m^3 \nu_M z_M C_{MX}]$$

Deybe-Hückel slope;
contains dielectric permittivity:
Fernández et al., 1997
Density by IAPWS-95

B and C contain adjustable parameters
Virial expansion for these parameters
Represent ion-ion interactions

Results for NaCl Brines





Pitzer based model …

- can be extended to other salts
- can be implemented into mixture model based on the routines developed for the seawater model

Take Away Messages

- Gibbs and Helmholtz energy based EOS have successfully been combined in an accurate multiparameter mixture model
- Pitzer model for the description of brines has been combined with a Helmholtz energy based reference EOS for water (IAPWS-95)
- **Accurate property models used for transport can (soon) be used to describe storage as well**
- **Interface problems (soon to be) overcome**

$$G(T,p,m) = m_\mathrm{w} G_\mathrm{w}(T,p) + n_\mathrm{Salt} G_\mathrm{Salt}(T,p) + G^\mathrm{EX}(T,p,m) + n_\mathrm{salt} \nu RT(\ln m - 1)$$

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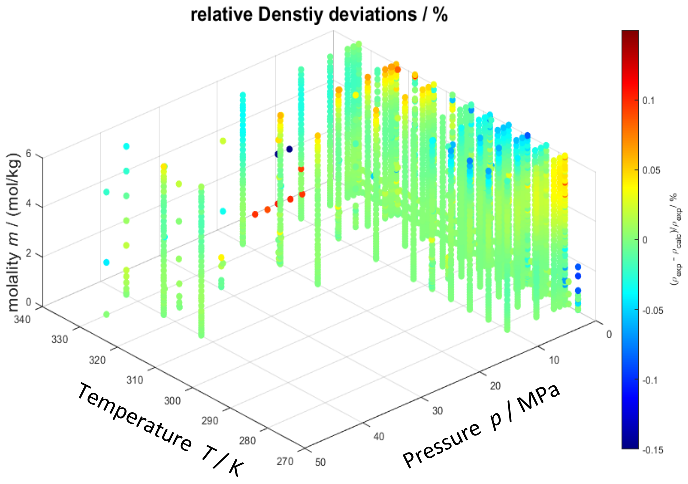

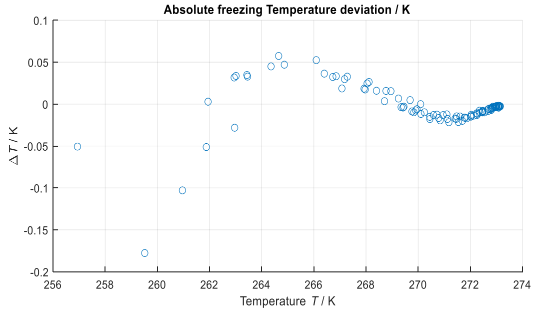

Acknowledgement

ACT ELEGANCY, Project No 271498, has received funding from DETEC (CH), FZJ/PtJ (DE), RVO (NL), Gassnova (NO), BEIS (UK), Gassco AS and Statoil Petroleum AS, and is cofunded by the European Commission under the Horizon 2020 programme, ACT Grant Agreement No 691712.