

Thermodynamic database development for Phase Change Materials

From Aqueous Solution to Pure Liquid Salt

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GTT Users' Meeting, TPH Herzogenrath, 27. June 2018



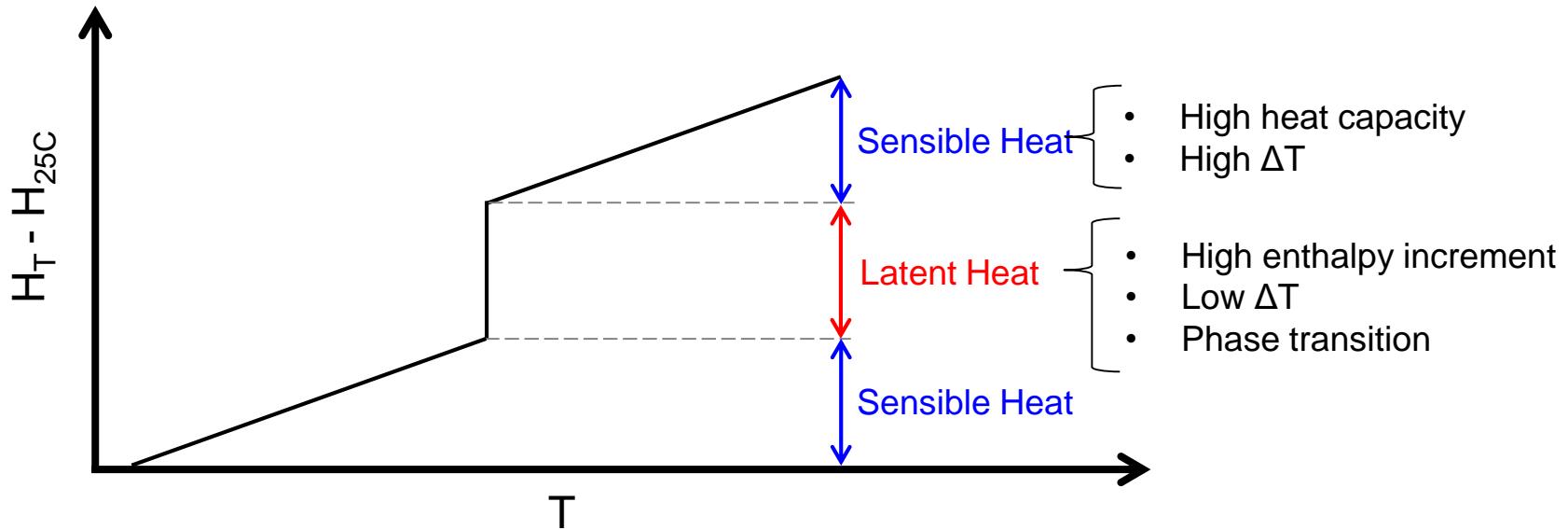
Outline

- PCM Screening
- Modelling
 - Models for Liquids
 - The H₂O-Zn(NO₃)₂ system
 - Ionic Species
 - Associate Species
 - Results
- Summary



PCM Screening

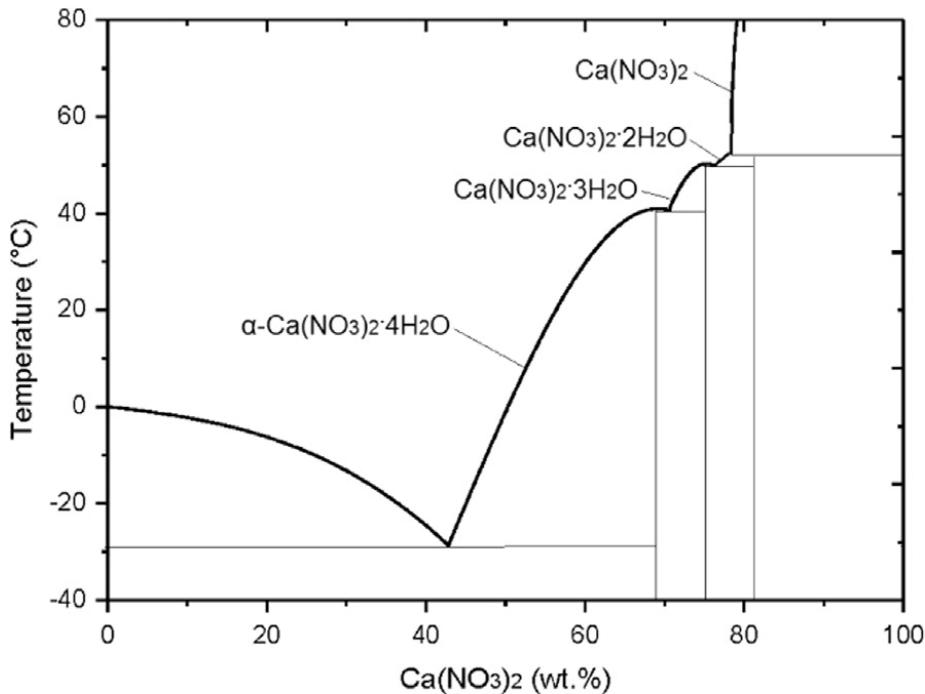
- Heat Storage Media



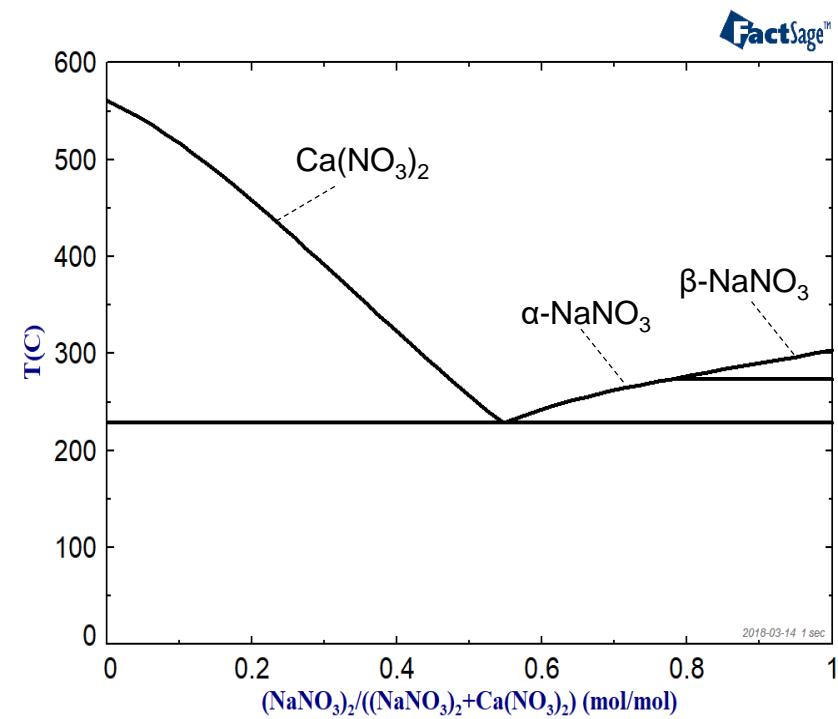
PCM Screening

- Application specific

Low temperature



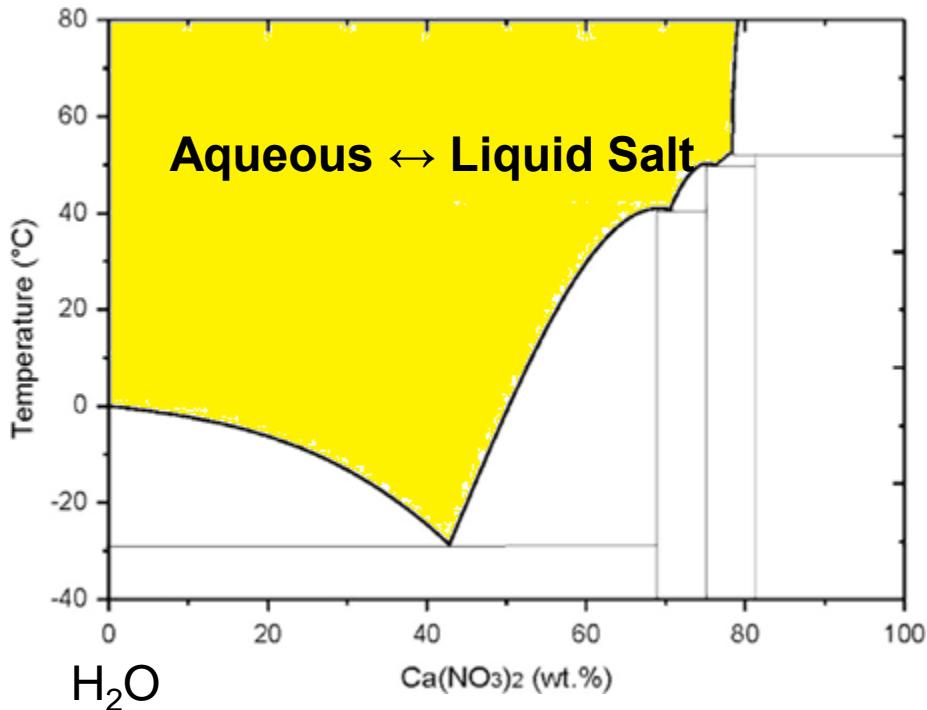
High temperature



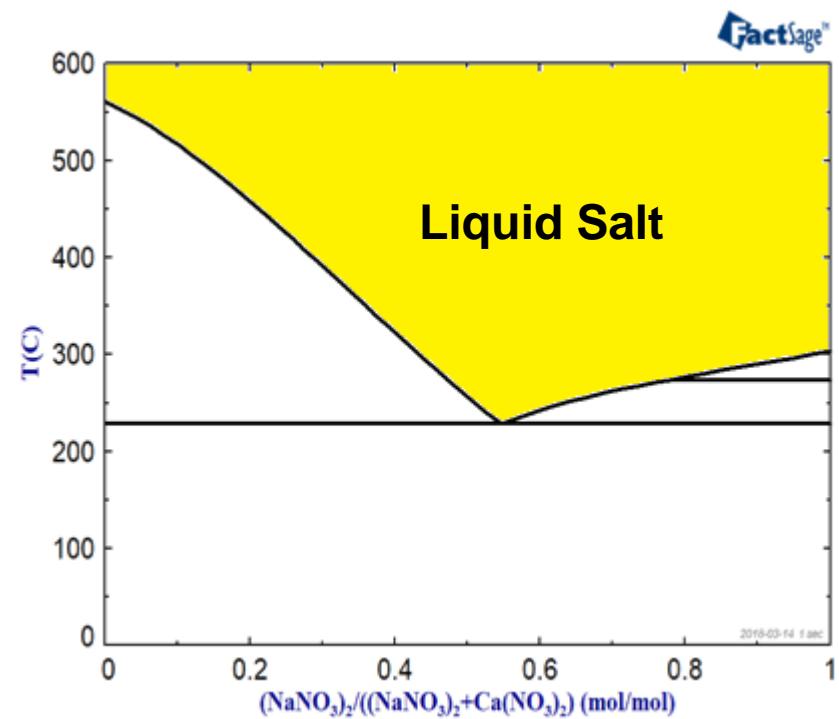
PCM Screening

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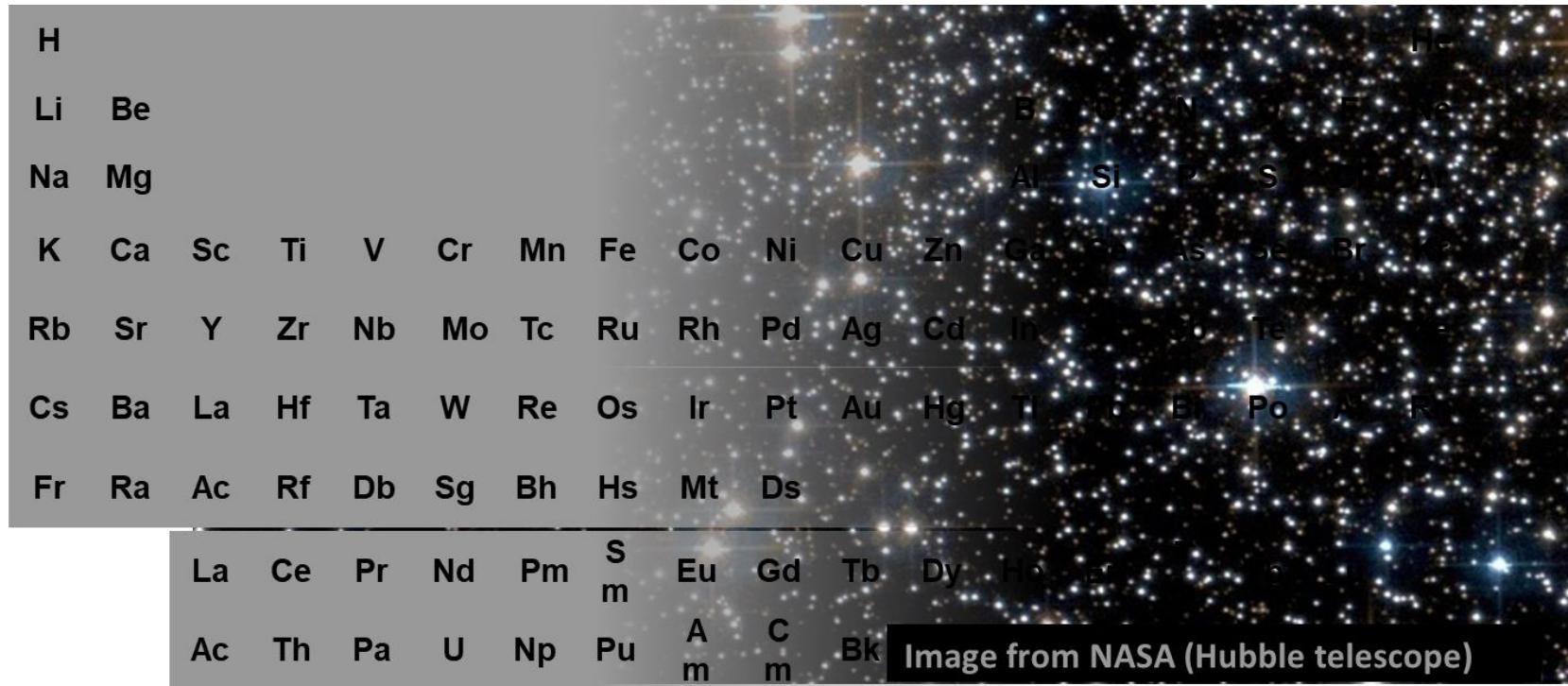
Low temperature



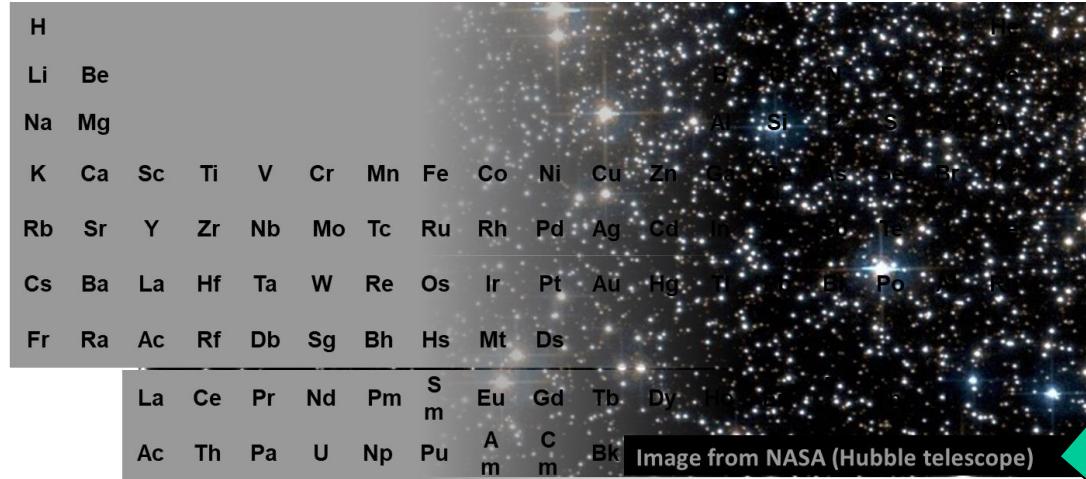
High temperature



Chemical Compound Space



Chemical Compound Space



Models for Aqueous/Liquid Solutions

- Pitzer

$$G_{\text{ex}}/RT = n_w \left[f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \right]$$

- Extended UNIQUAC

$$G^E = G_{SR}^E + G_{LR}^E = G_{\text{Combinatorial}}^E + G_{\text{Residual}}^E + G_{\text{Debye-Hückel}}^E$$

- Redlich-Kister Polynomial

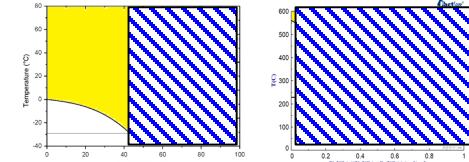
$$G_m^E(T, x_i) = \sum_i \sum_{j \prec i} x_i x_j \sum_{\nu=0}^{n_{ij}} L_{ij}^{(\nu)}(T) (x_i - x_j)^\nu + \sum_i \sum_{j \prec i} \sum_{k \prec j} x_i x_j x_k (x_i L_i^{ijk}(T) + x_j L_j^{ijk}(T) + x_k L_k^{ijk}(T)) / (x_i + x_j + x_k)$$



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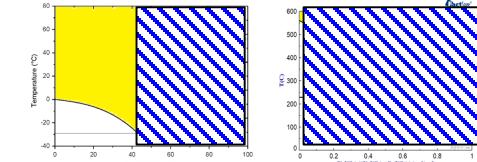
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Models for Aqueous/Liquid Solutions

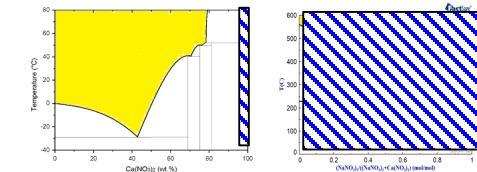
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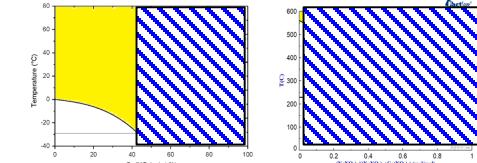
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Models for Aqueous/Liquid Solutions

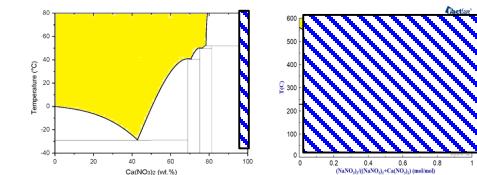
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$$G_{\text{ex}}/RT = n_w \left[f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \right]$$



- Extended UNIQUAC

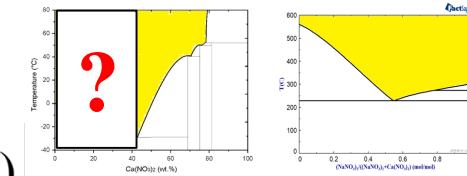
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=f(Ionic Strength)

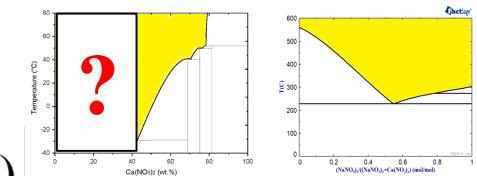
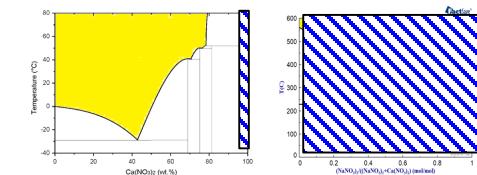
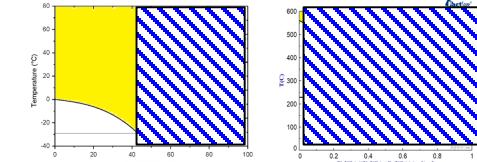
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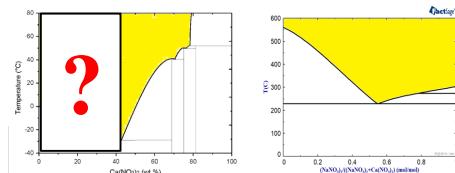
Models for Aqueous/Liquid Solutions

*Can the Aqueous Solution be modelled without
a Debye-Hückel type term?*

- Redlich-Kister Polynomial

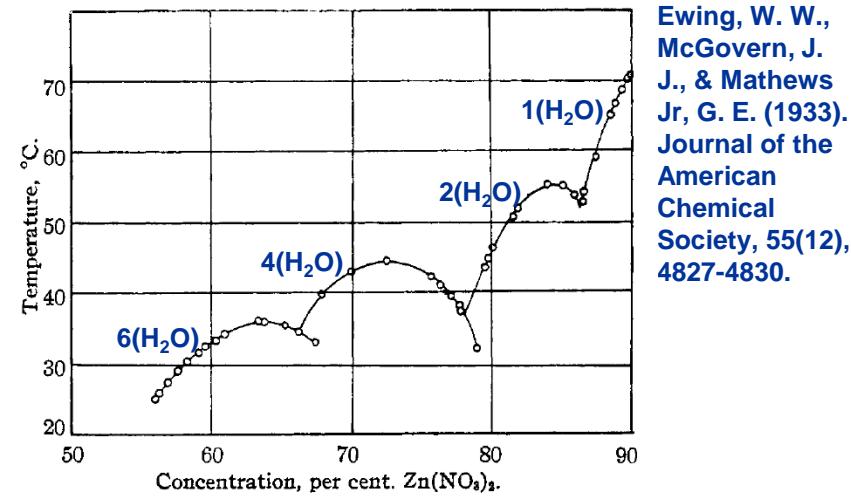
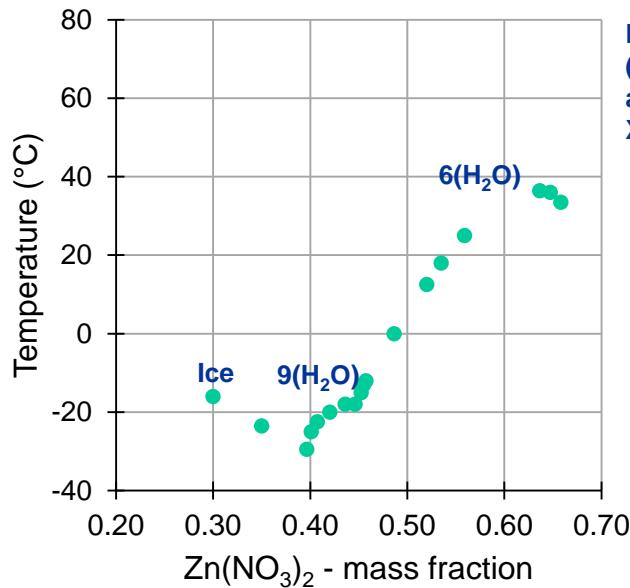
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The $\text{H}_2\text{O}-\text{Zn}(\text{NO}_3)_2$ system

- Solid-Liquid Equilibria



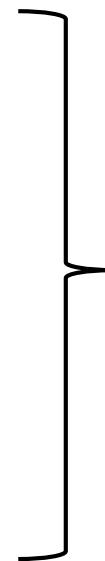
H₂O-Zn(NO₃)₂: Liquid Solution

- Dissociation of water
- Dissociation of Zn(OH)2
- Dissociation of HNO3
- Hydrates as associates
- Interaction parameters



H₂O-Zn(NO₃)₂: Liquid Solution

- Dissociation of water
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- Dissociation of HNO₃
- Hydrates as associates
- Interaction parameters



Non-Ideal
Associate Species
Model



Dissociation of Water

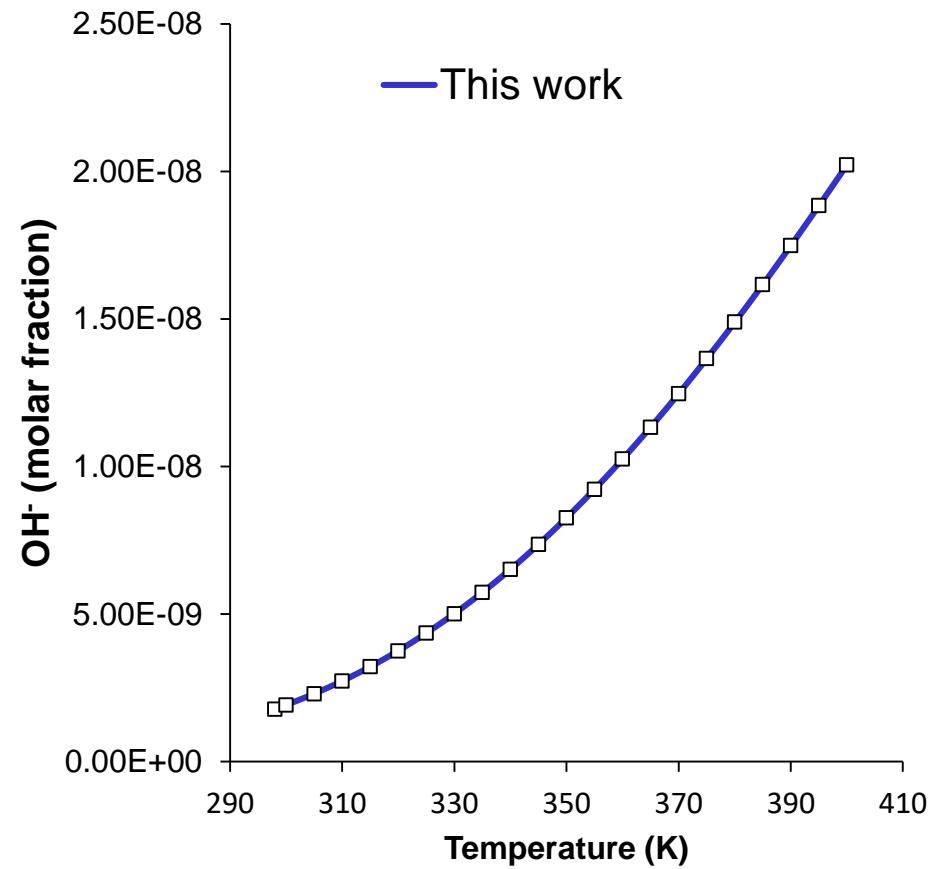


- $G^\circ(\text{H}^+) = \frac{1}{2}G^\circ(\text{H}_{2(\text{gas})})^{\text{FactPS}}$
 - $\text{H}_{2(\text{gas})} \leftrightarrow \text{H}^+ + \text{e}^-$
- $G^\circ(\text{OH}^-)$ optimized to reproduce $[\text{OH}^-]^{\text{Aqueous Ideal}}$ from:
 - 1 mol H_2O between 25 and 100°C

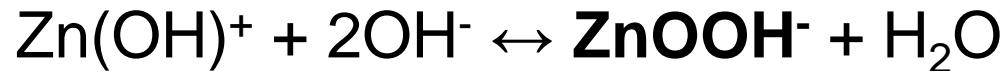
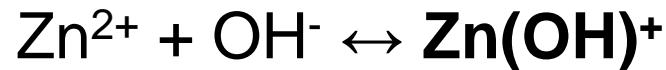
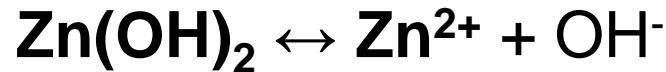


G°(OH⁻) Optimization

- Equilibrium for 1 mol H₂O (25 to 100°C)
- $H^\circ(OH^-) = -230 \text{ kJ/mol}$
- $S^\circ(OH^-) = -143 \text{ kJ/K.mol}$
- $C_P(OH^-) = -125 \text{ kJ/K.mol}$



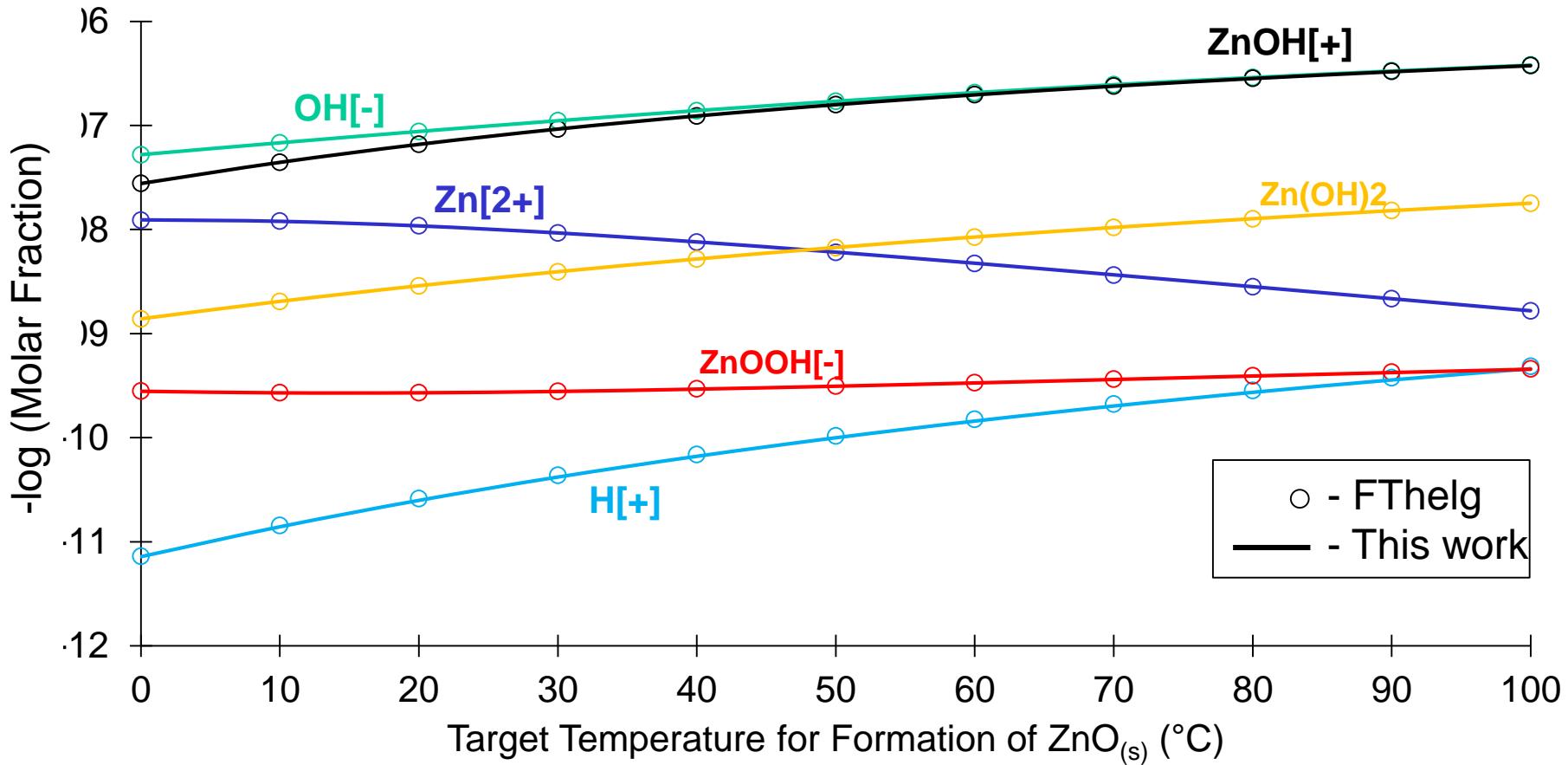
Dissociation of Zn(OH)2



- $G^\circ(\text{Zn(OH)}_2)$
 - $G^\circ(\text{Zn}^{2+})$
 - $G^\circ(\text{Zn(OH)}^+)$
 - $G^\circ(\text{ZnOOH}^-)$
- Optimized



Dissociation of Zn(OH)₂



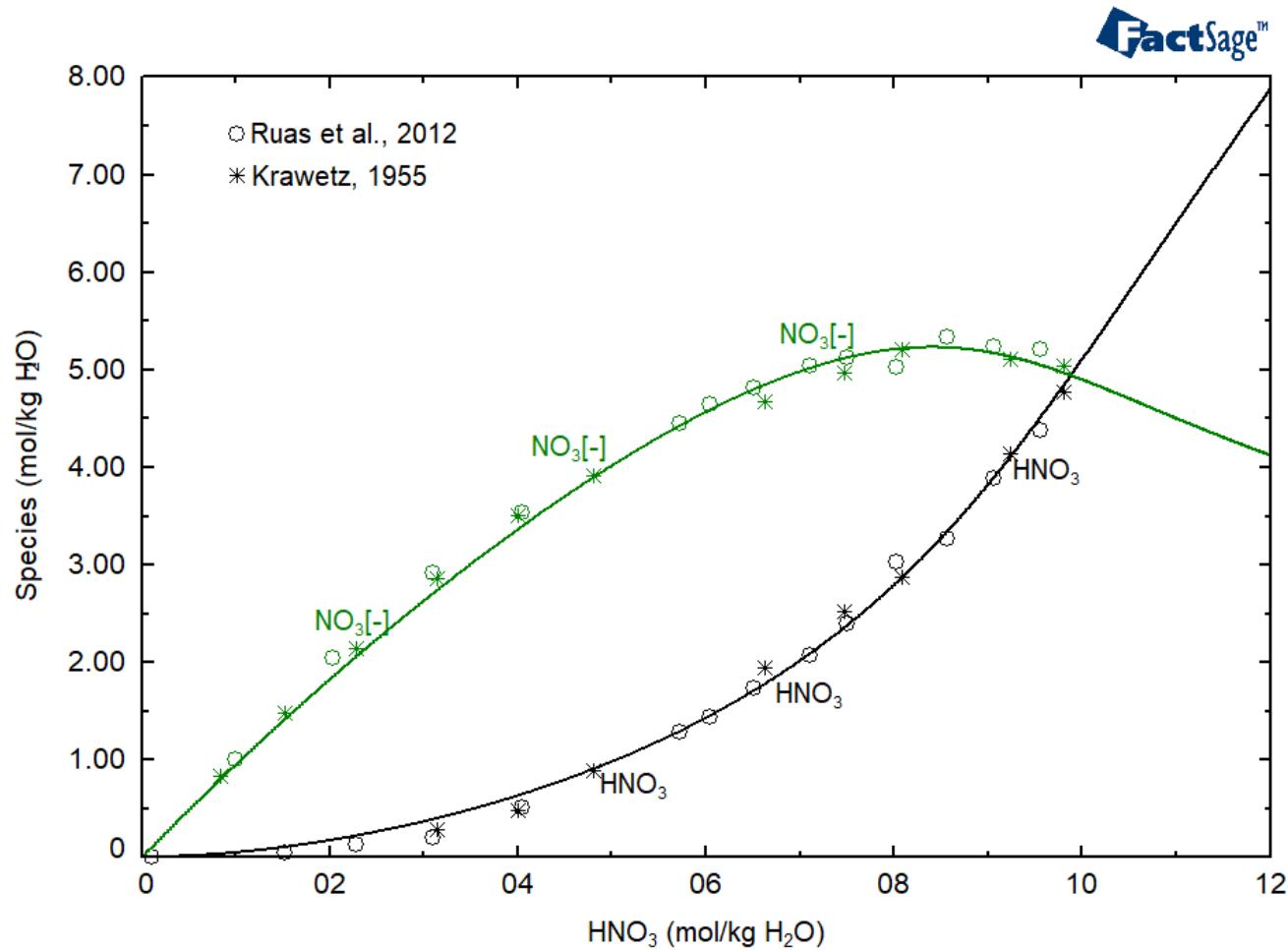
Dissociation of HNO₃



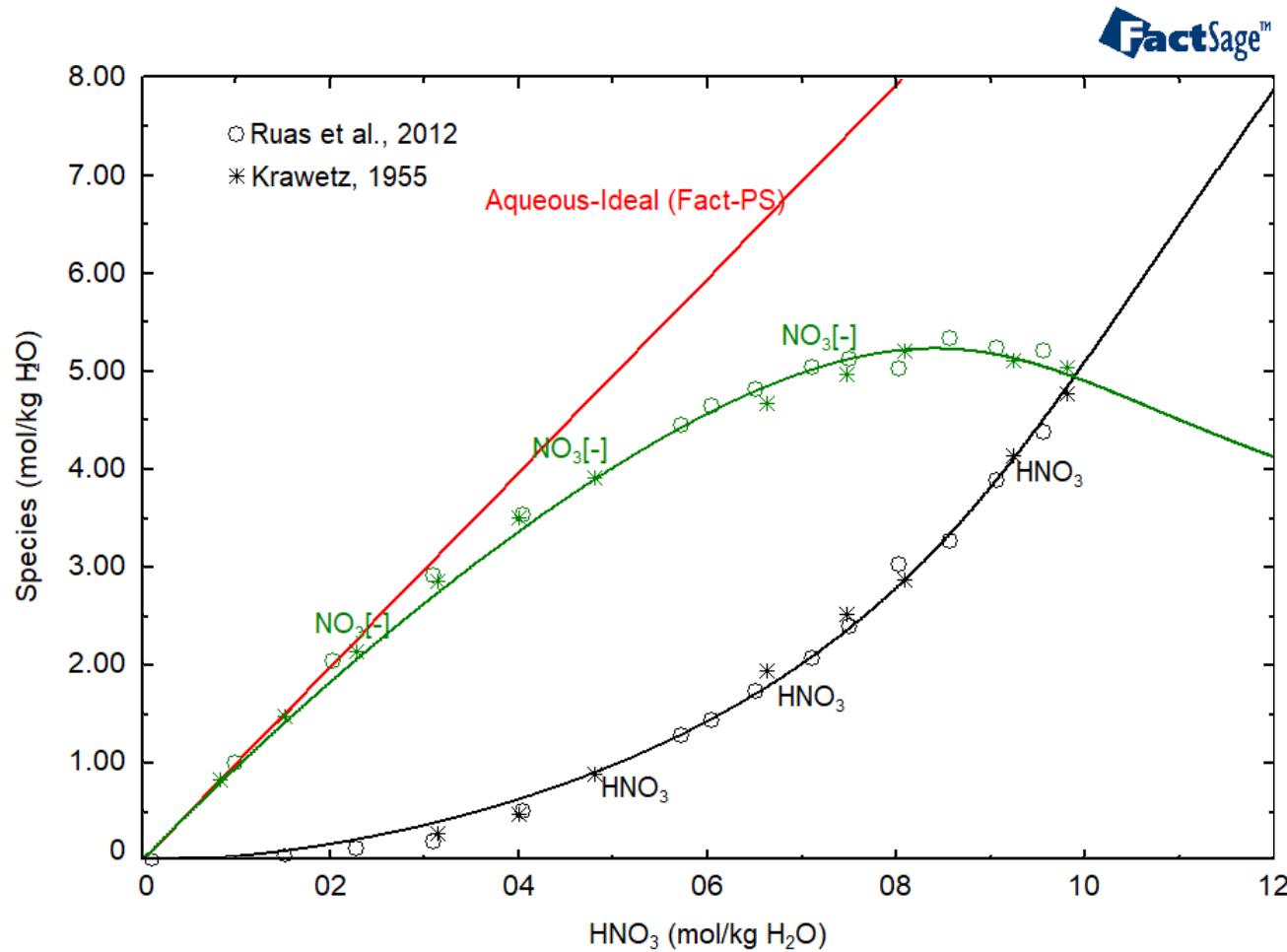
- G°(HNO_{3(l)}) from FactPS
 - G°(NO₃⁻)
 - L°(H₂O-HNO₃)
 - L^{HNO3}(H⁺-HNO₃-NO₃⁻)
 - L^{H2O}(H⁺-H₂O-NO₃⁻)
- Optimized



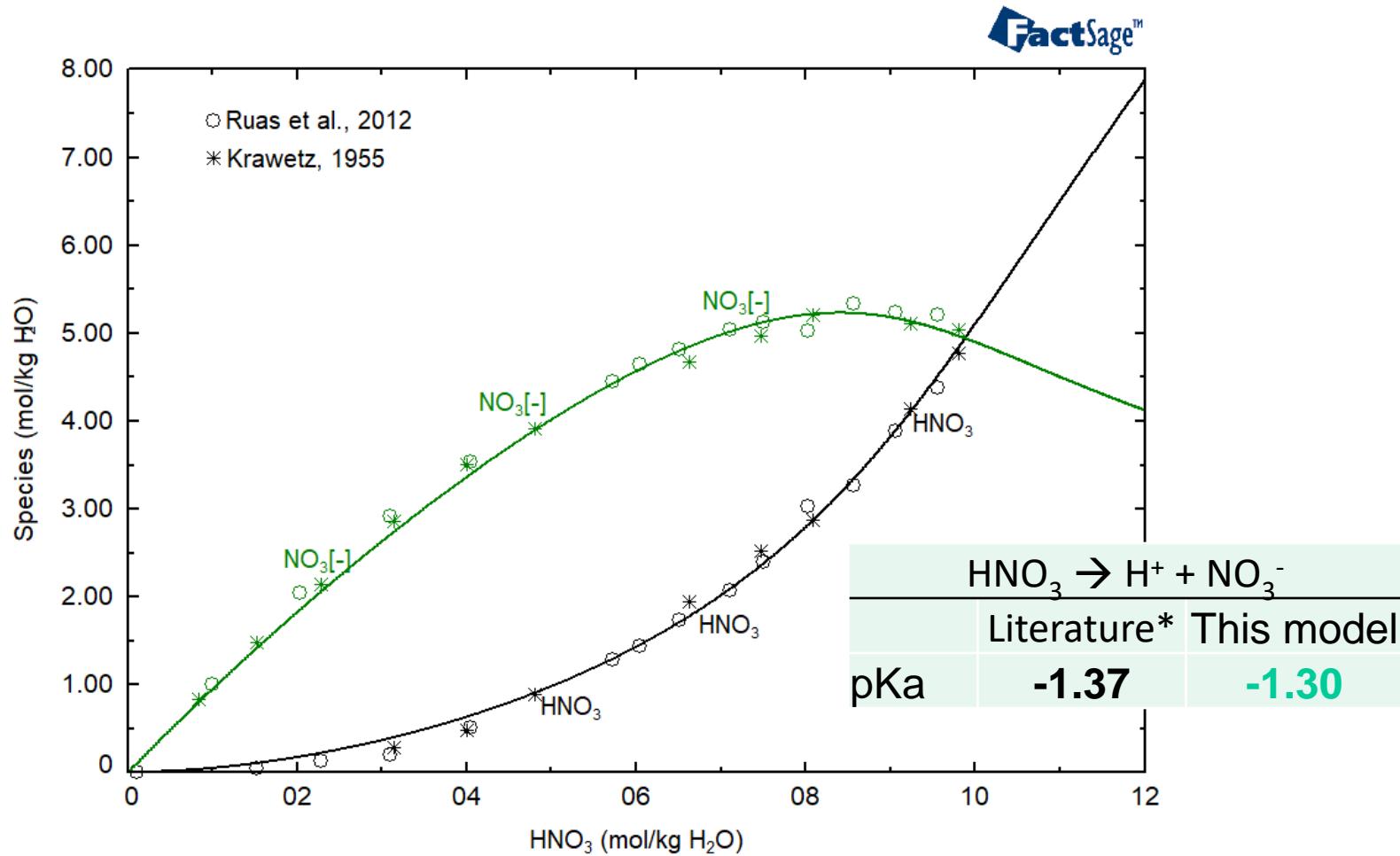
Dissociation of HNO_3



Dissociation of HNO_3



Dissociation of HNO_3



* - Rodríguez-Ruiz, I., Teychené, S., Vitry, Y., Biscans, B., & Charton, S. (2018). Thermodynamic modeling of neodymium and cerium oxalates reactive precipitation in concentrated nitric acid media. *Chemical Engineering Science*, 183, 20-25.



Hydrate as Associate

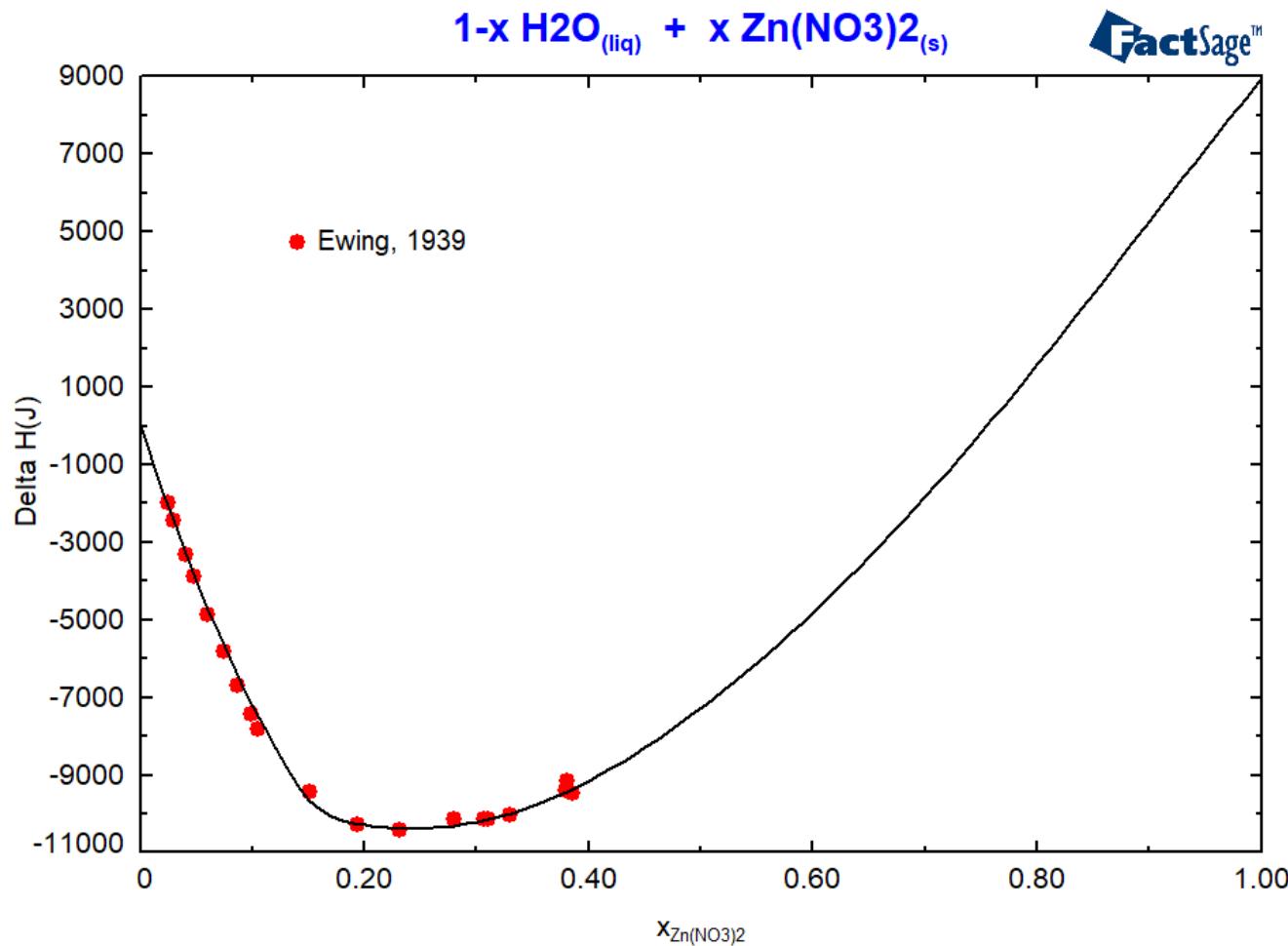
- Associate
 - Tetrahydrate: $\text{Zn}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})_{(\text{liq})}$

$$G^\circ(\text{Zn}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})_{(\text{liq})}) = G^\circ(\text{Zn}(\text{NO}_3)_2) + 4^*G^\circ(\text{H}_2\text{O})_{(\text{liq})} + \Delta_r G^\circ$$

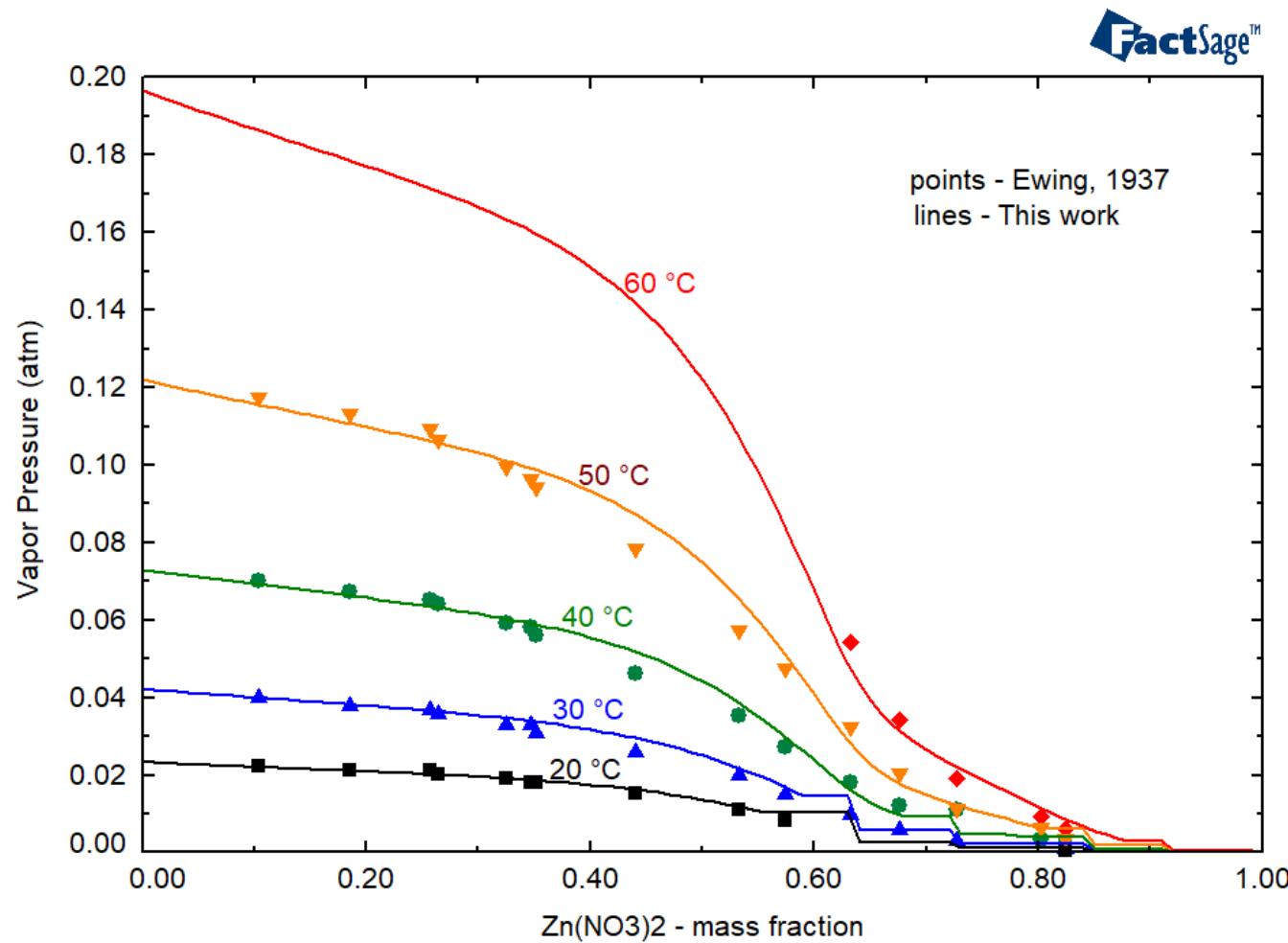
- $\Delta_r G^\circ$
 - $L^{0,1}(\text{H}_2\text{O}-\text{Zn}(\text{NO}_3)_2)$
 - $L^{0,1}(\text{H}_2\text{O}-\text{Assoc.})$
 - $L^{0,1}(\text{Assoc.}-\text{Zn}(\text{NO}_3)_2)$
- Optimized



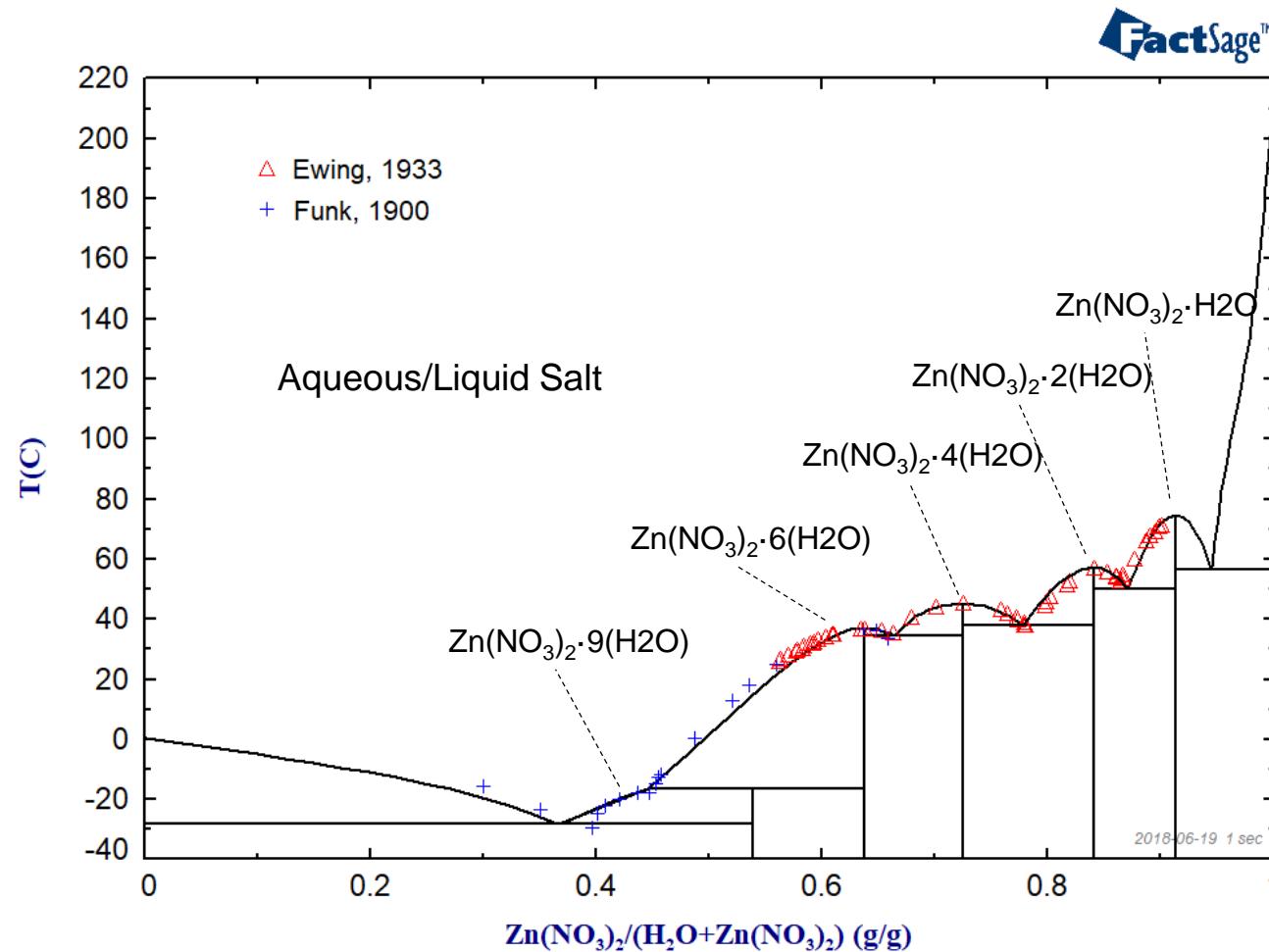
H₂O-Zn(NO₃)₂: Heat of Mixing at 25°C



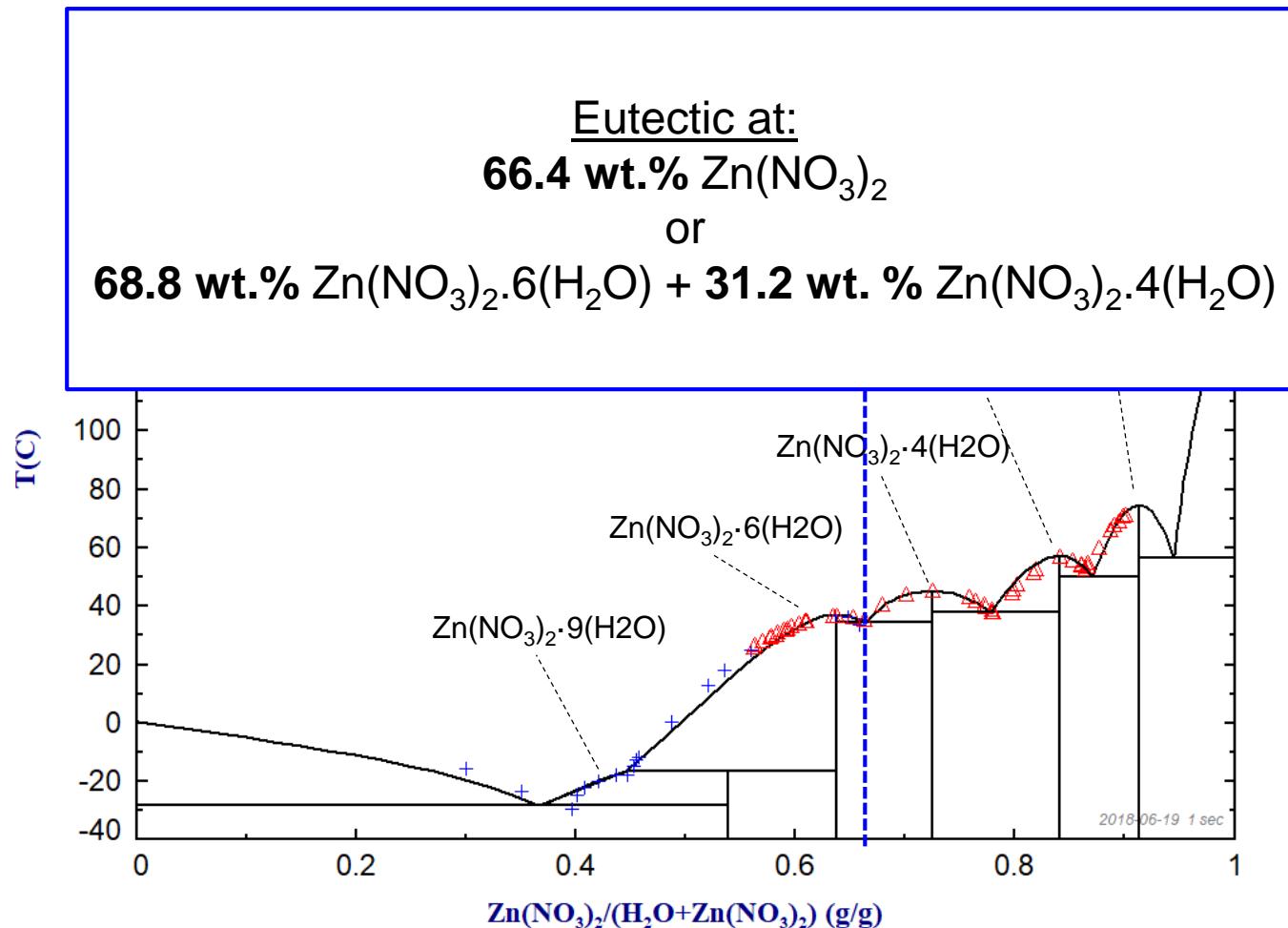
$\text{H}_2\text{O-Zn}(\text{NO}_3)_2$: Vapor Pressure = $f(x, T)$



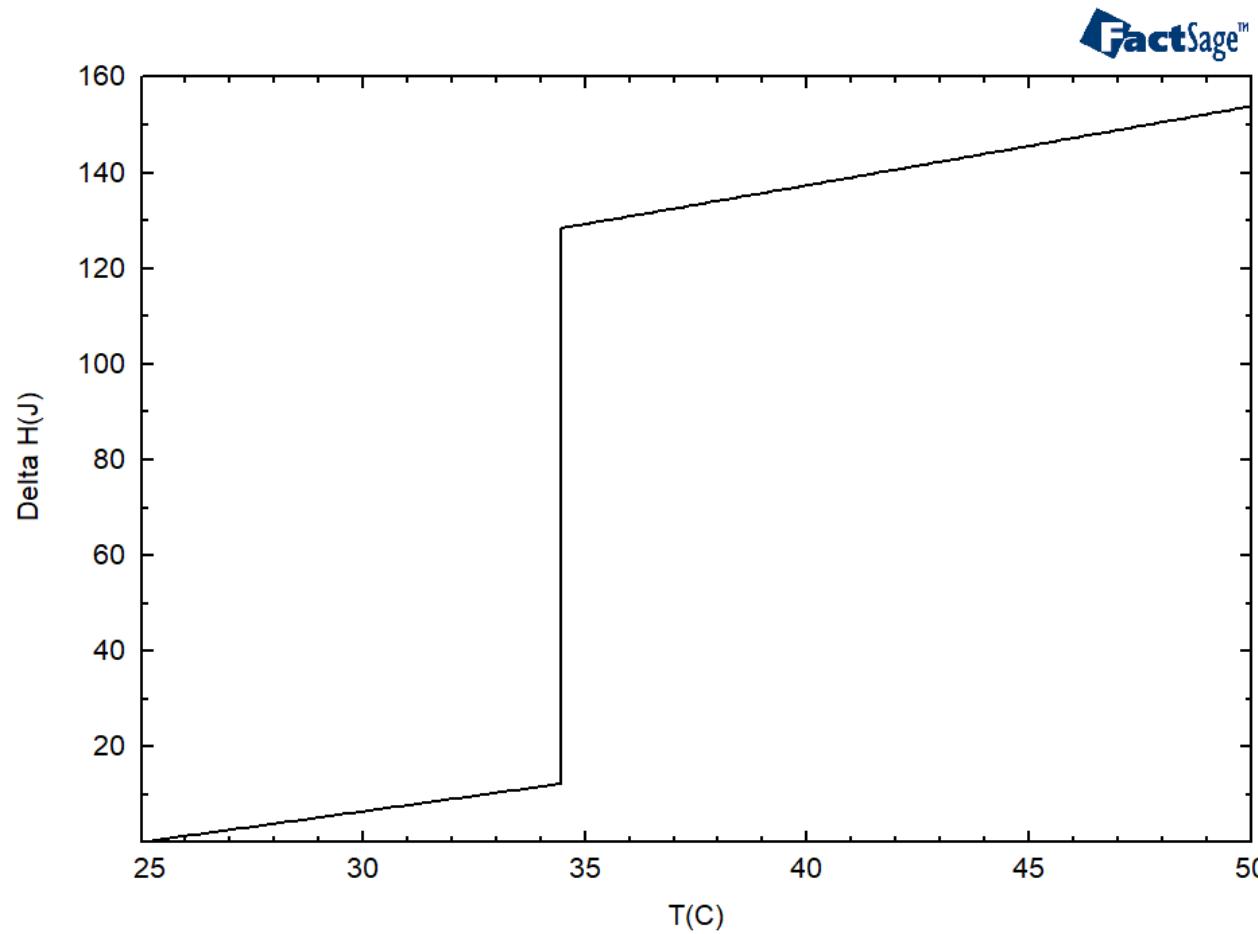
H₂O-Zn(NO₃)₂: Phase Diagram



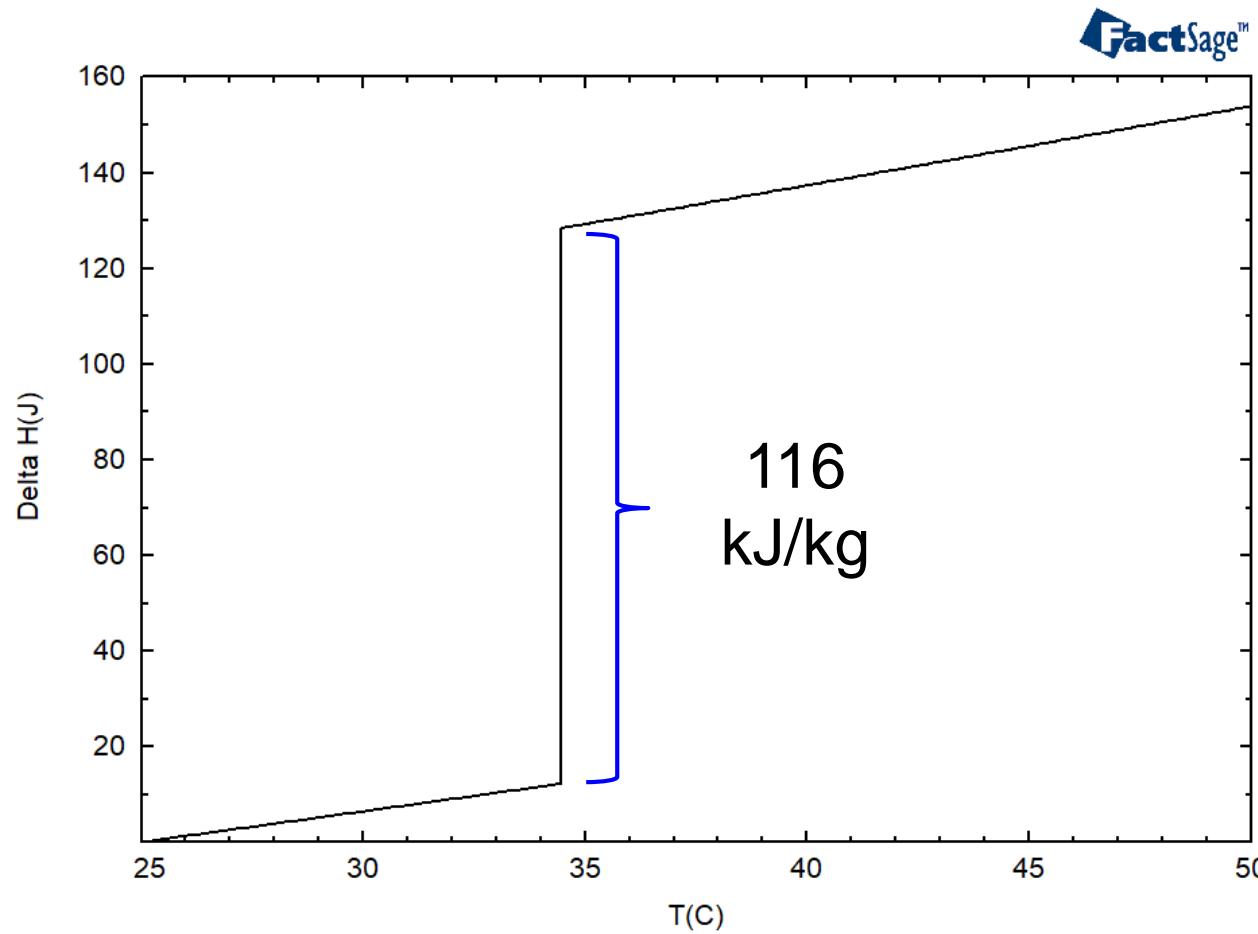
H₂O-Zn(NO₃)₂: Phase Diagram



$H_T - H_{25C}$: Eutectic at 66.4 wt.% Zn(NO₃)₂



$H_T - H_{25C}$: Eutectic at 66.4 wt.% Zn(NO₃)₂



Summary

- Aqueous Solution successfully described by the Non-Ideal Associate Species model, **without a Debye-Hückel type term**
- $\text{H}_2\text{O-Zn}(\text{NO}_3)_2$ system assessed with a single consistent model for the liquid solution **within its entire composition range**
- This approach enables salt systems to be coupled with hydrated salt systems freely
- Higher prospects of identifying suitable eutectic mixtures to function as Phase Change Materials



Thank You

GTT Users' Meeting, TPH Herzogenrath, 27. June 2018

Bruno Reis

