Thermodynamic database development for Phase Change Materials

From Aqueous Solution to Pure Liquid Salt

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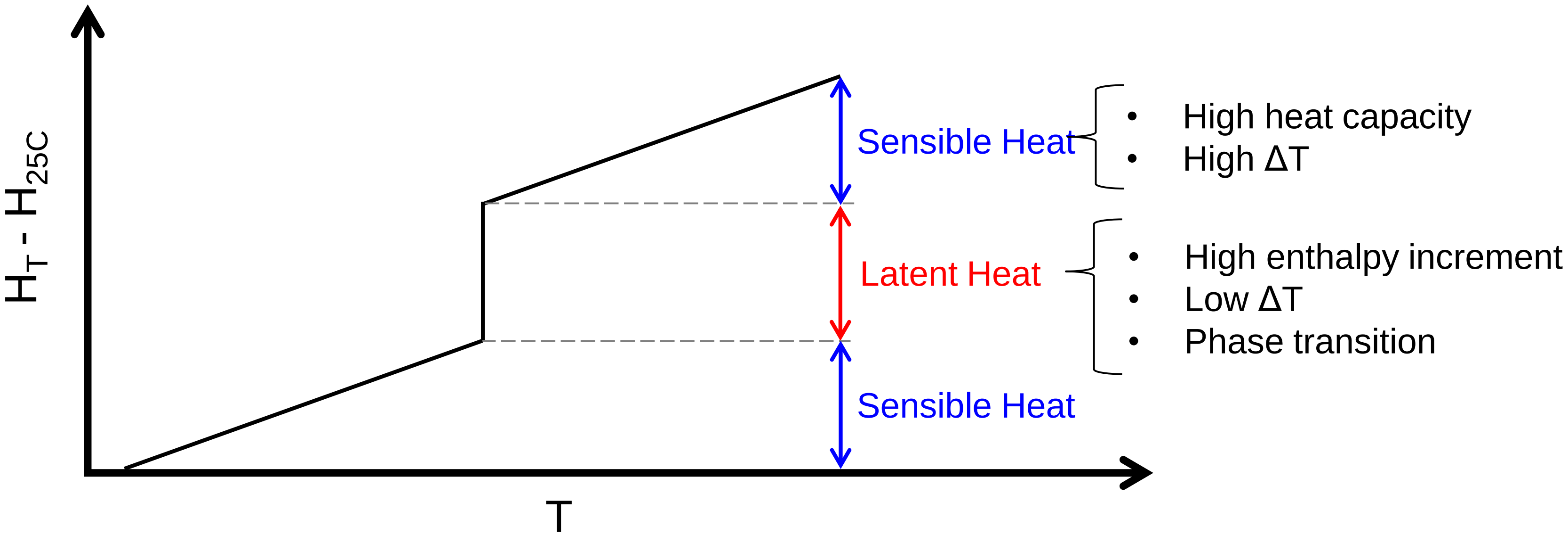
GTT Users‘ Meeting, TPH Herzogenrath, 27. June 2018

Outline

- PCM Screening
- Modelling
  - Models for Liquids
  - The H_2O-$Zn(NO_3)_2$ system
  - Ionic Species
  - Associate Species
  - Results
- Summary

PCM Screening

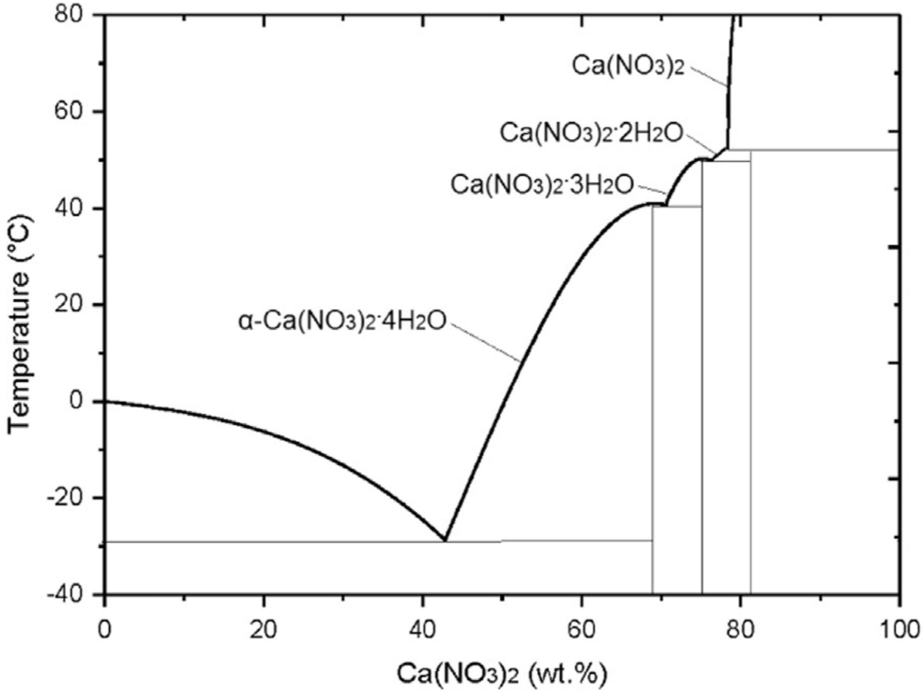
- Heat Storage Media



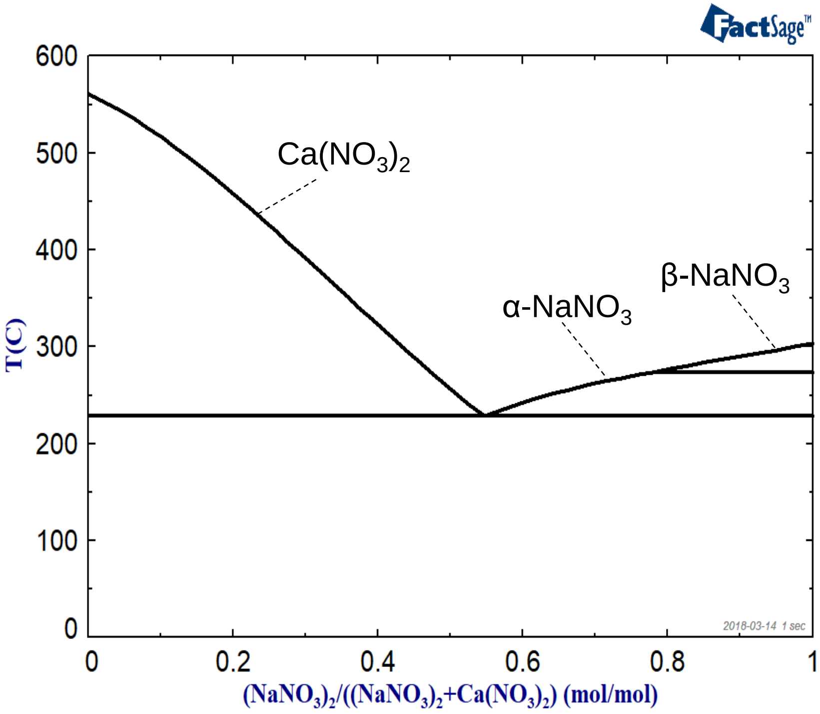
PCM Screening

- Application specific

Low temperature



High temperature



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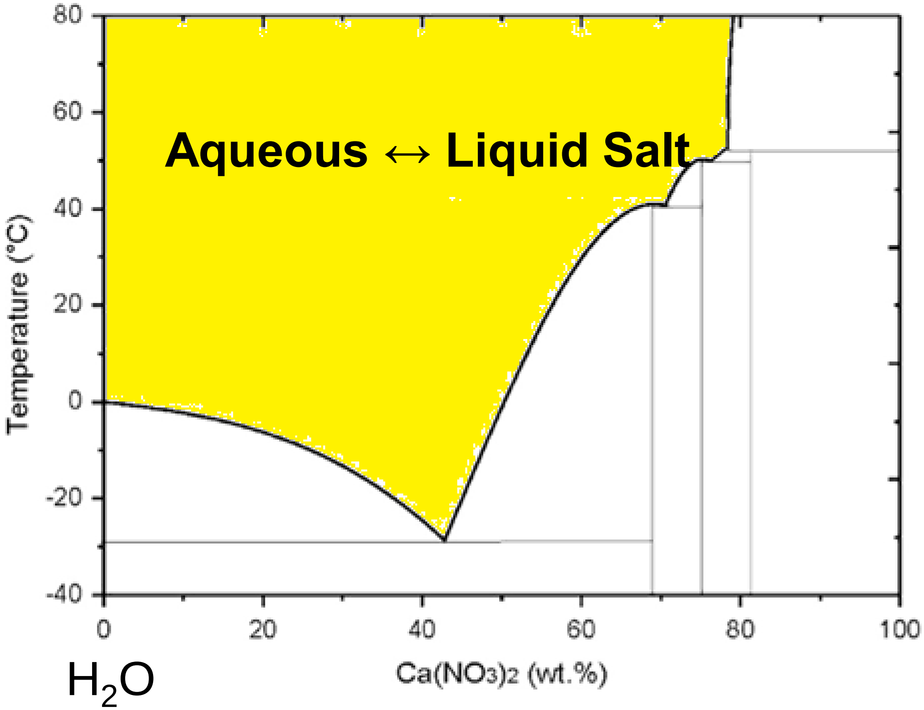

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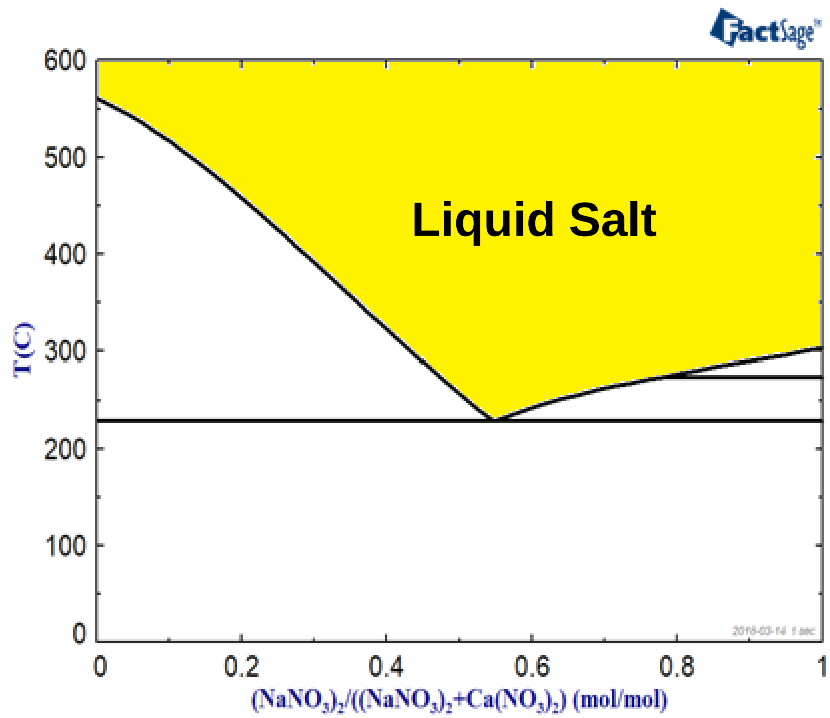

Chemical Compound Space

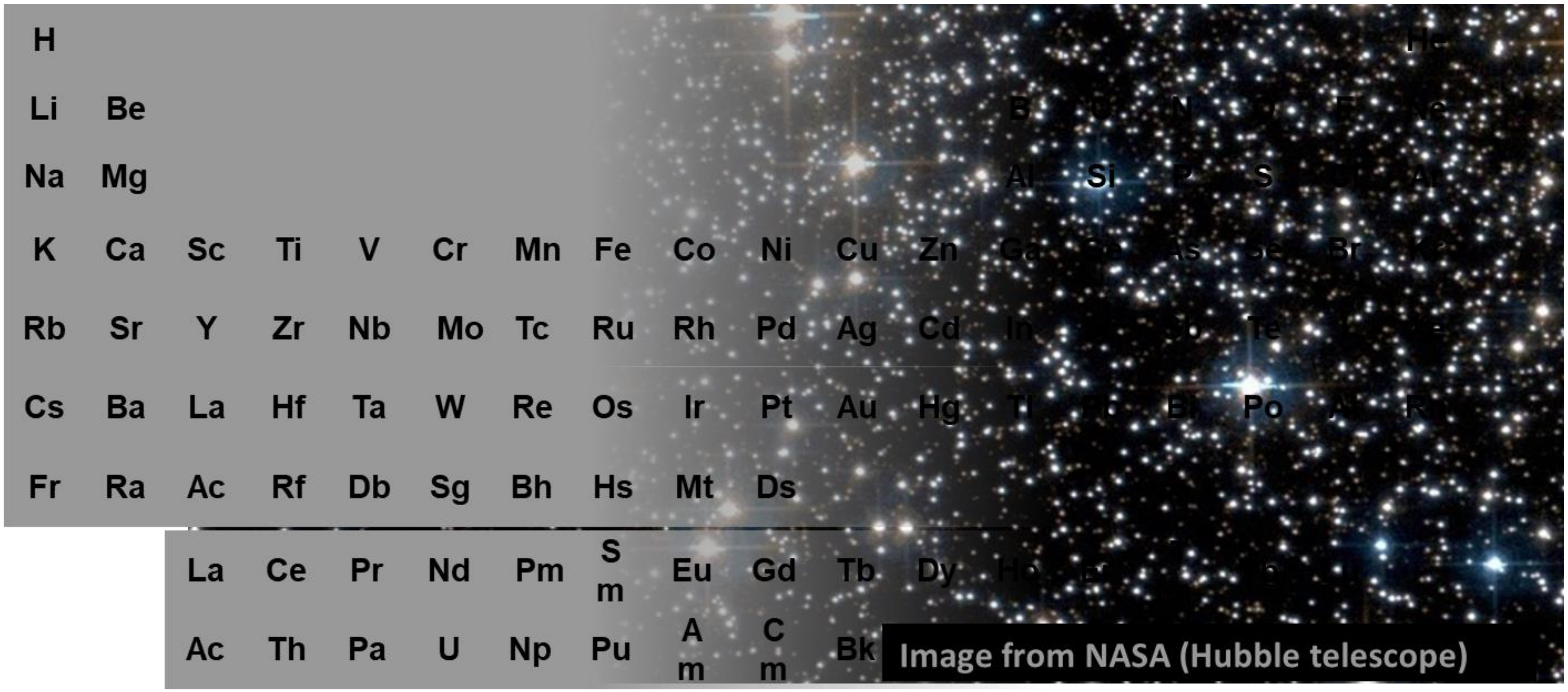

Image from NASA (Hubble telescope)

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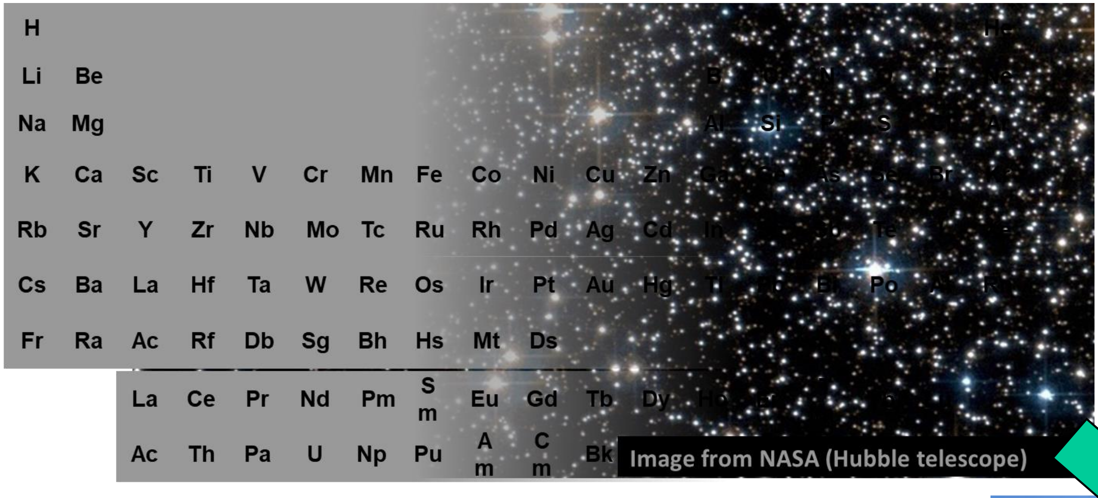

Image from NASA (Hubble telescope)

Models for Aqueous/Liquid Solutions

- Pitzer

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

- Extended UNIQUAC

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

- Redlich-Kister Polynomial

$$G^E_m(T, x_i) = \sum_i \sum_{\prec j} x_i x_j \sum_{\nu=0}^{n_{ij}} L^{(\nu)}_{ij}(T)(x_i - x_j)^\nu$$
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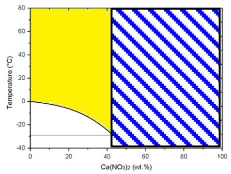

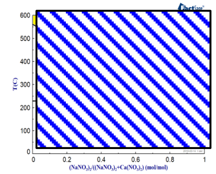

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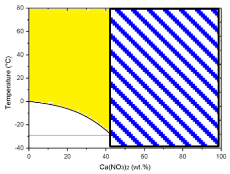

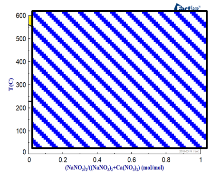

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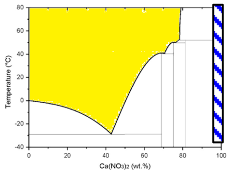

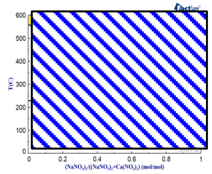

- Redlich-Kister Polynomial

$$G_m^E(T, x_i) = \sum_i \sum_{\prec j} x_i x_j \sum_{\nu=0}^{n_{ij}} L_{ij}^{(\nu)}(T)(x_i - x_j)^\nu$$

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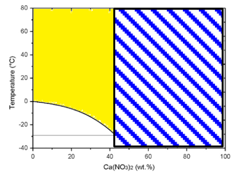

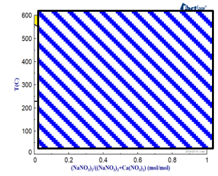

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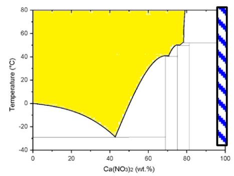

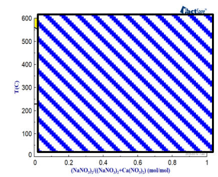

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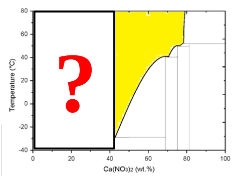

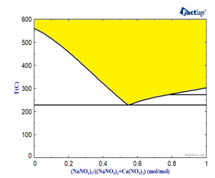

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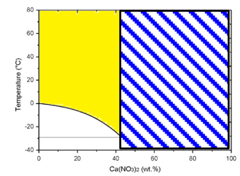
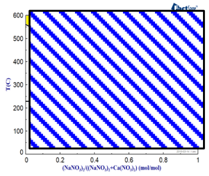
=f(Ionic Strength)





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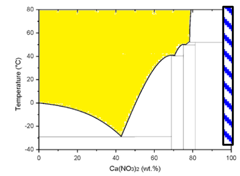

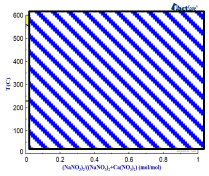

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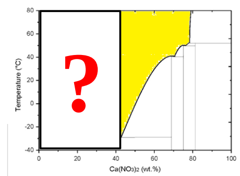

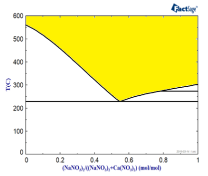

Models for Aqueous/Liquid Solutions

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

- Redlich-Kister Polynomial

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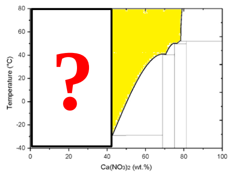
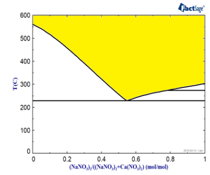
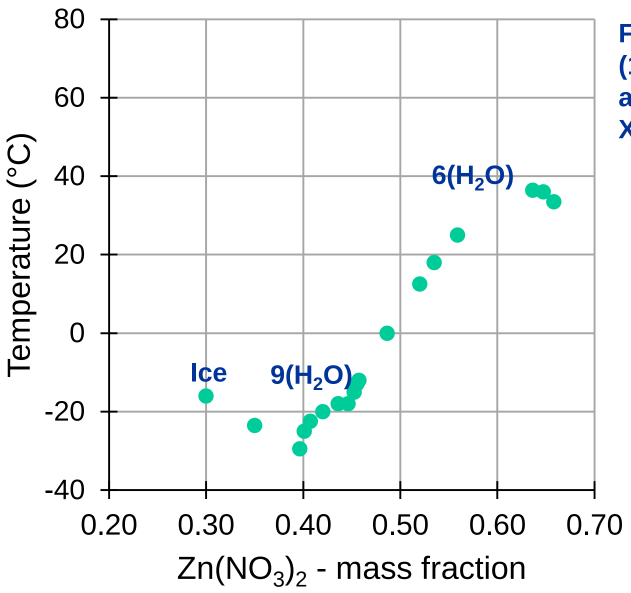


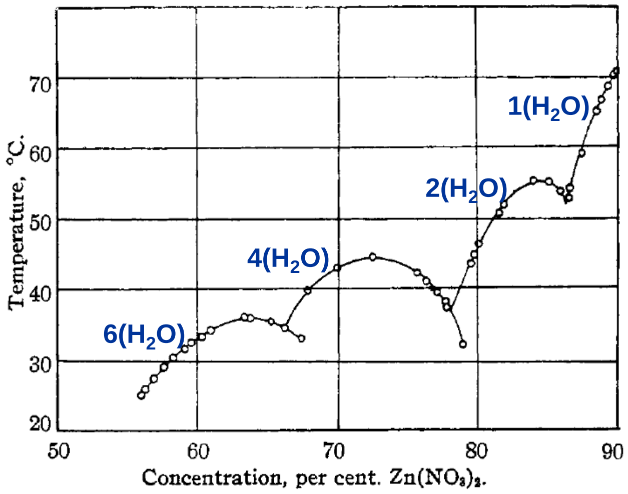


The H_2O-$Zn(NO_3)_2$ system

- Solid-Liquid Equilibria



Funk, R. (1900). Z. anorg. Chem., XX, 393-418.



Ewing, W. W., McGovern, J. J., & Mathews Jr, G. E. (1933). Journal of the American Chemical Society, 55(12), 4827-4830.

H_2O-$Zn(NO_3)_2$: Liquid Solution

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

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} Non-Ideal Associate Species Model

Dissociation of Water

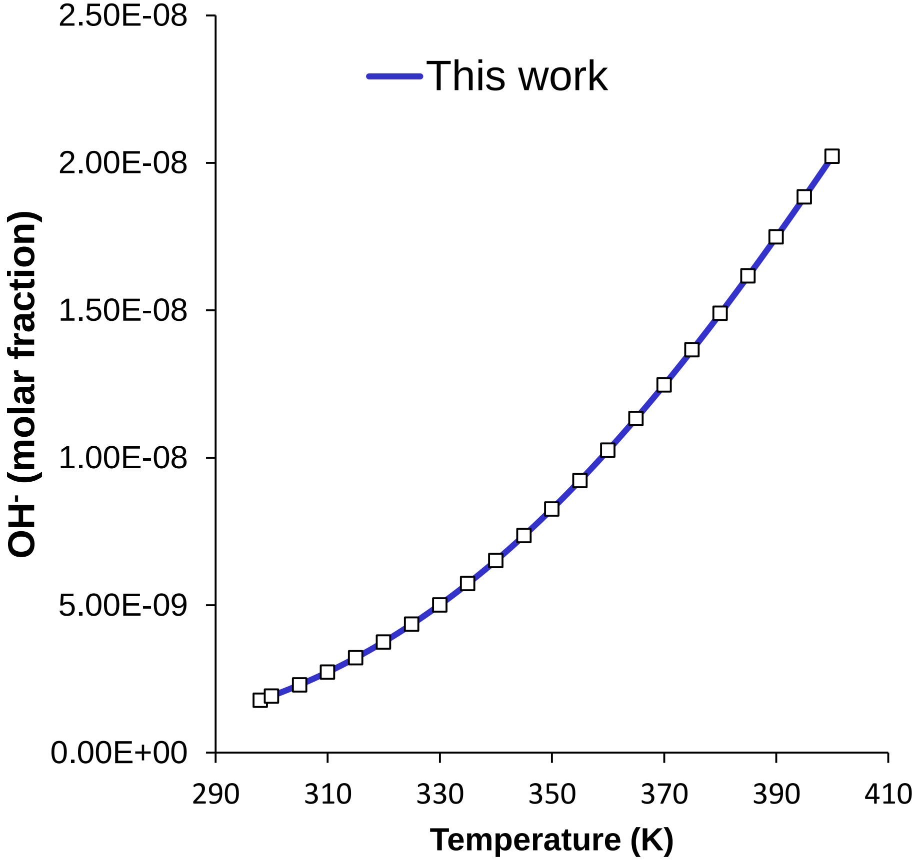
$$H_2O \leftrightarrow H^+ + OH^-$$

- $G°(H^+) = ½G°(H_{2(gas)})^{FactPS}$
  - $H_{2(gas)} \leftrightarrow H^+ + e^-$
- $G°(OH^-)$ optimized to reproduce $[OH^-]^{\text{Aqueous Ideal}}$ from:
  - 1 mol H_2O between 25 and 100°C

G°(OH⁻) Optimization

- Equilibrium for 1 mol H_2O (25 to 100°C)

- $H°(OH^-)$ = -230 kJ/mol
- $S°(OH^-)$ = -143 kJ/K.mol
- $C_P(OH^-)$ = -125 kJ/K.mol



Dissociation of Zn(OH)2

$$\mathbf{Zn(OH)_2} \leftrightarrow \mathbf{Zn^{2+}} + OH^-$$

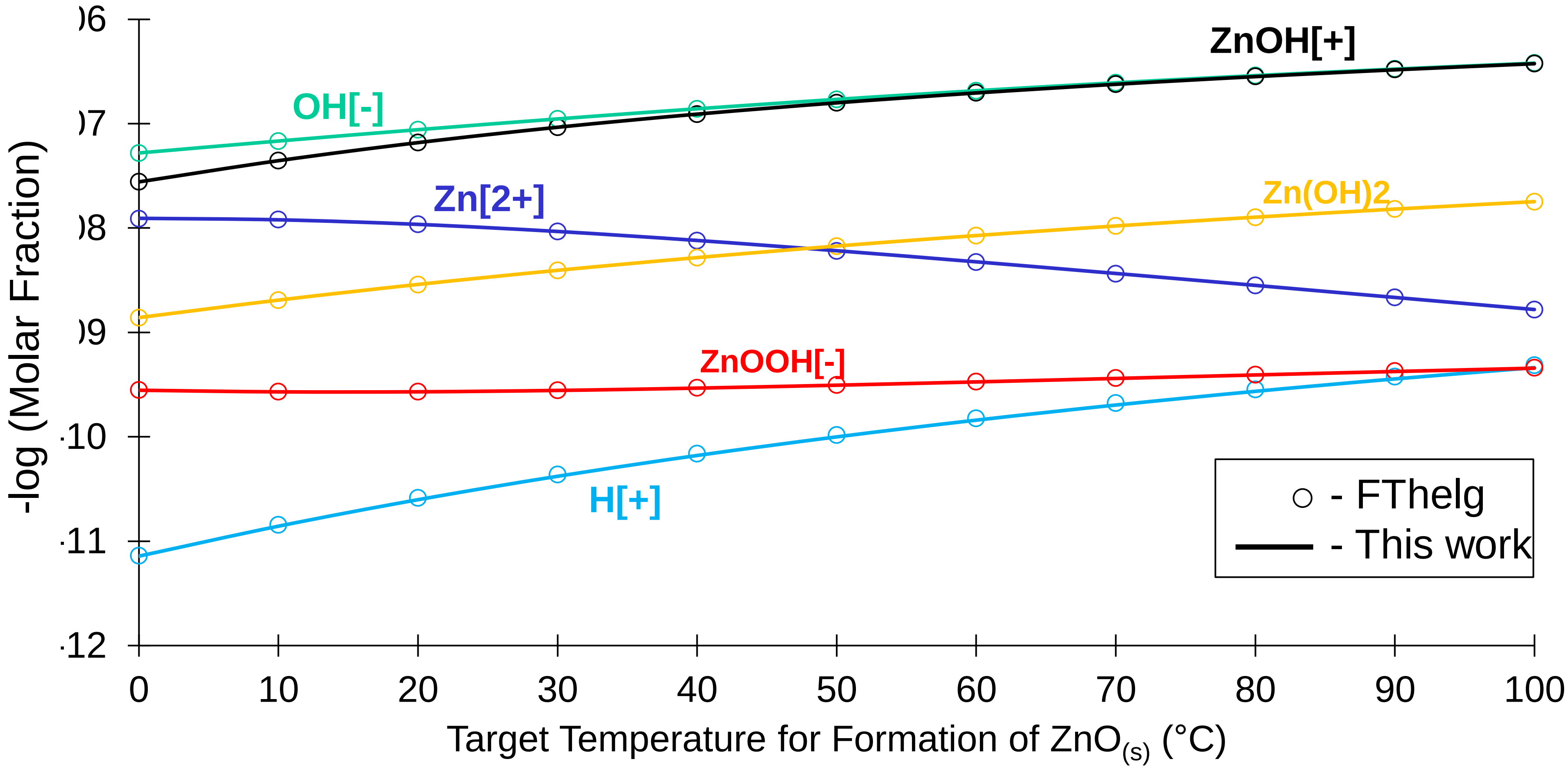
$$Zn^{2+} + OH^- \leftrightarrow \mathbf{Zn(OH)^+}$$

$$Zn(OH)^+ + 2OH^- \leftrightarrow \mathbf{ZnOOH^-} + H_2O$$

- $G°(Zn(OH)_2)$
- $G°(Zn^{2+})$
- $G°(Zn(OH)^+)$
- $G°(ZnOOH^-)$

} Optimized

Dissociation of Zn(OH)2



Dissociation of HNO_3

$$HNO_3 \leftrightarrow H^+ + NO_3^-$$

- $G°(HNO_{3(liquid)})$ from FactPS

- $G°(NO_3^-)$
- $L^0(H_2O\text{-}HNO_3)$
- $L^{HNO3}(H^+\text{-}HNO_3\text{-}NO_3^-)$
- $L^{H2O}(H^+\text{-}H_2O\text{-}NO_3^-)$

} Optimized

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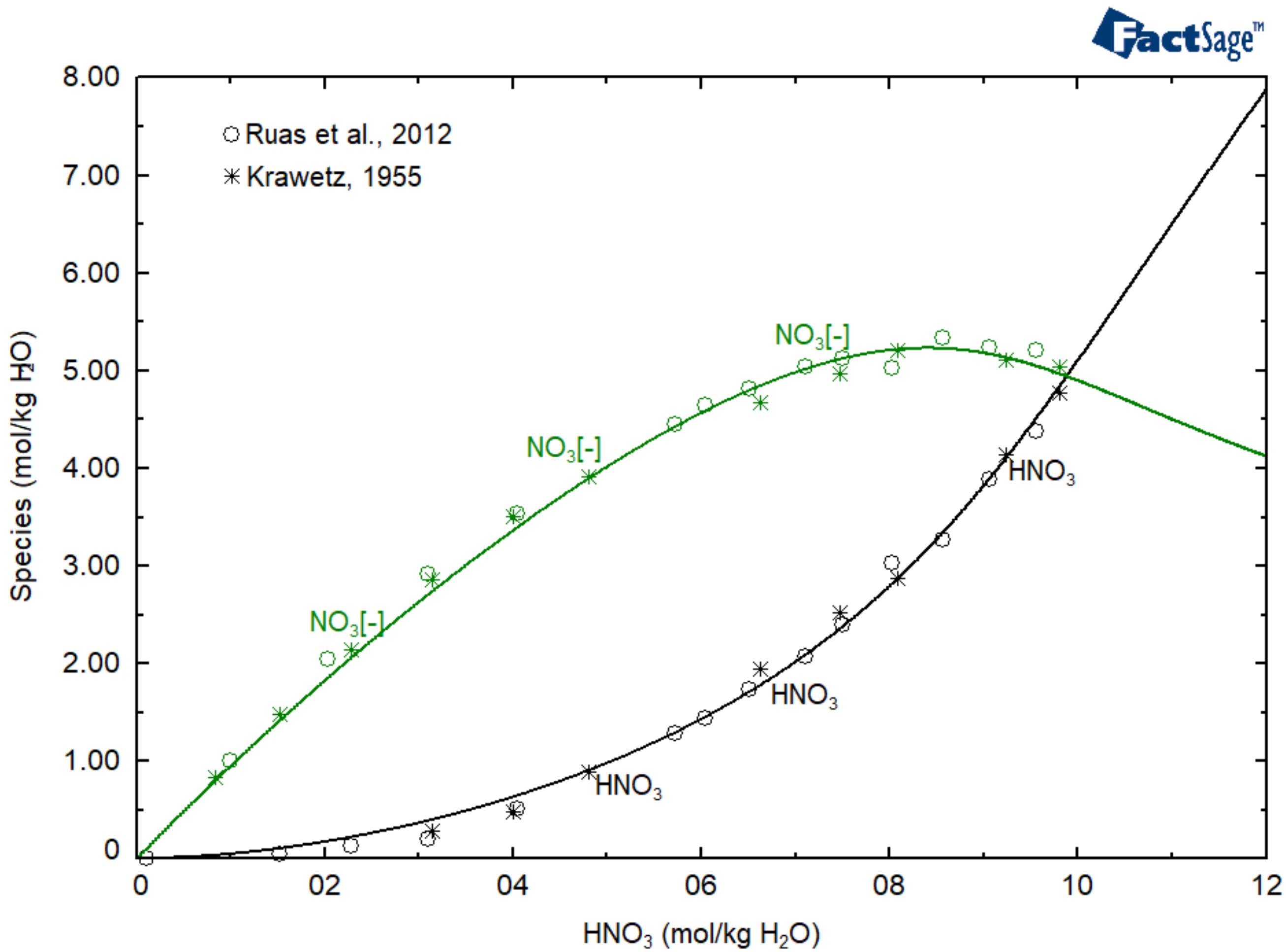

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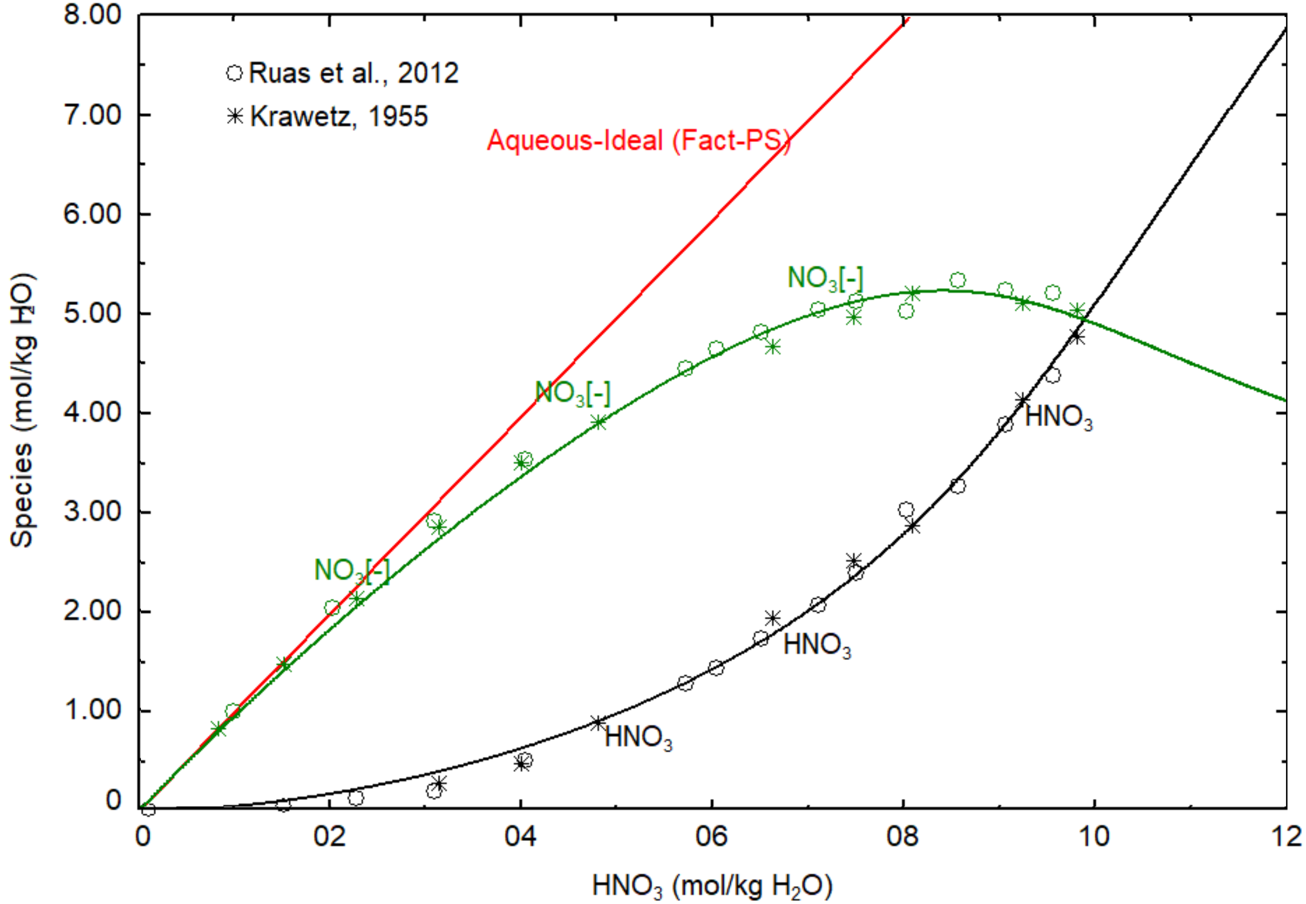

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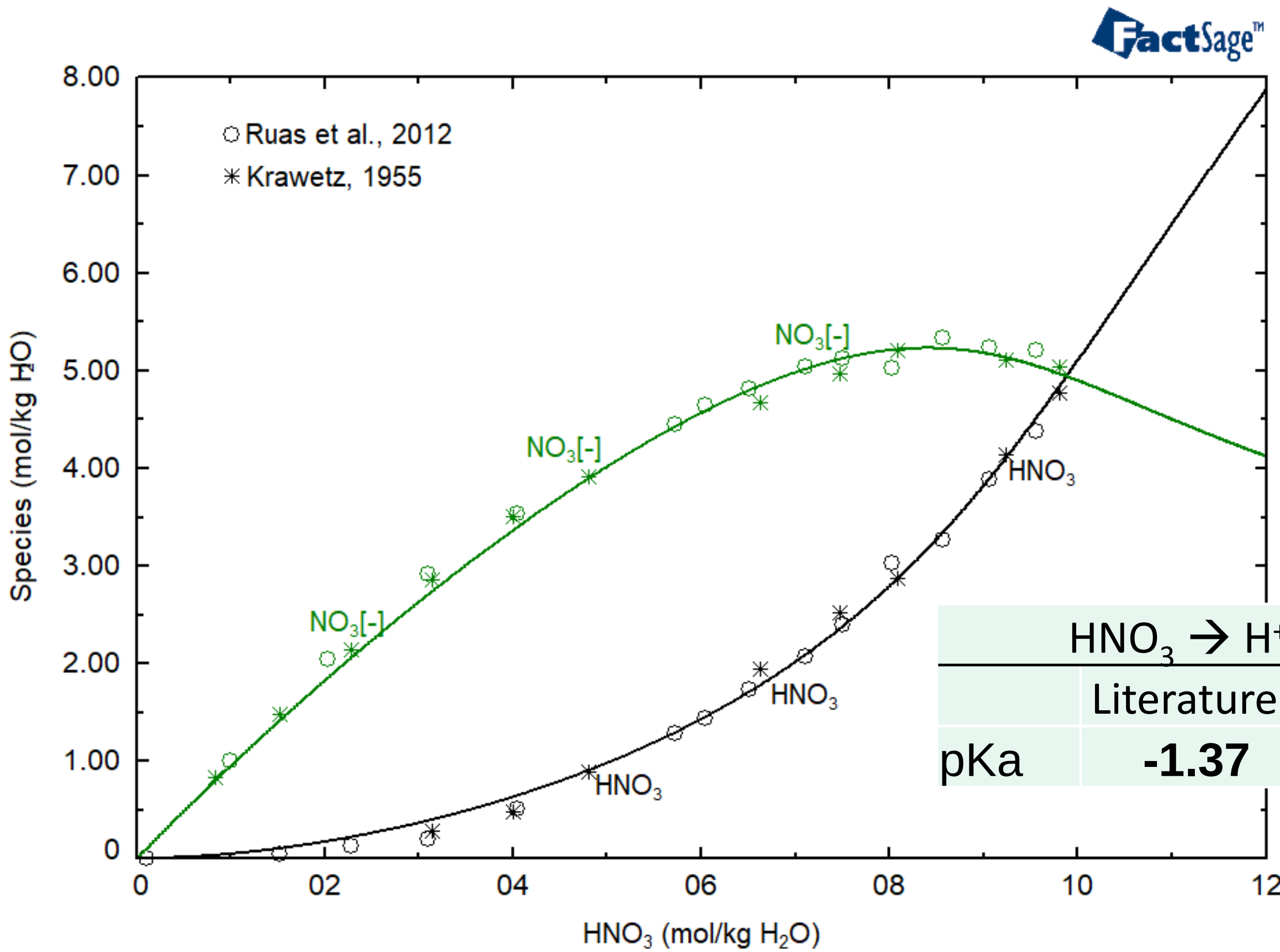


$HNO_3 \rightarrow H^+ + NO_3^-$		
	Literature*	This model
pKa	**-1.37**	**-1.30**

* - 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

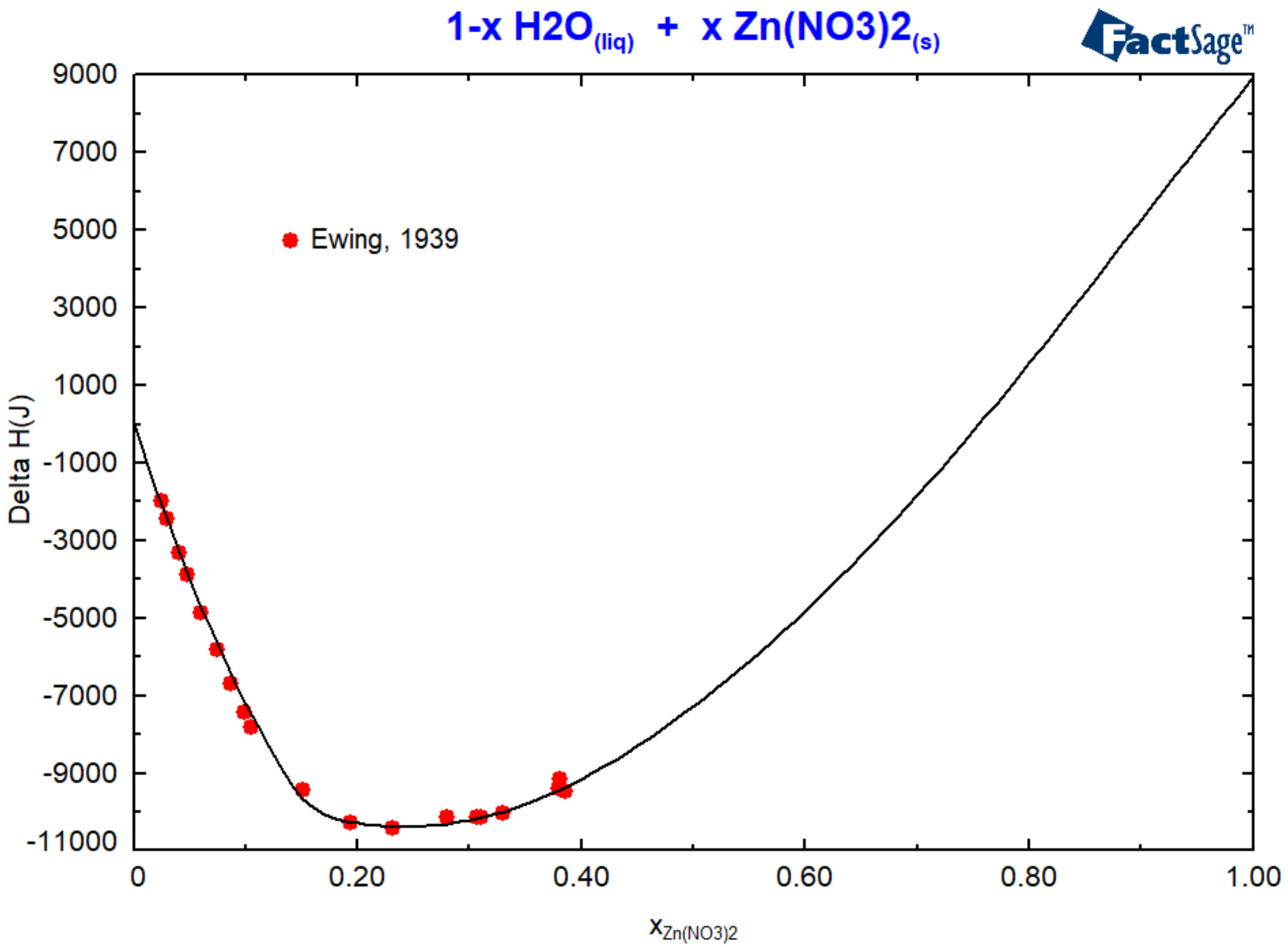
- Associate
  - Tetrahydrate: $Zn(NO_3)_2\cdot 4(H_2O)_{(liq)}$

$$G°(Zn(NO_3)_2\cdot 4(H_2O)_{(liq)}) = G°(Zn(NO_3)_{2(liq)}) + 4*G°(H_2O)_{(liq)} + \Delta_r G°$$

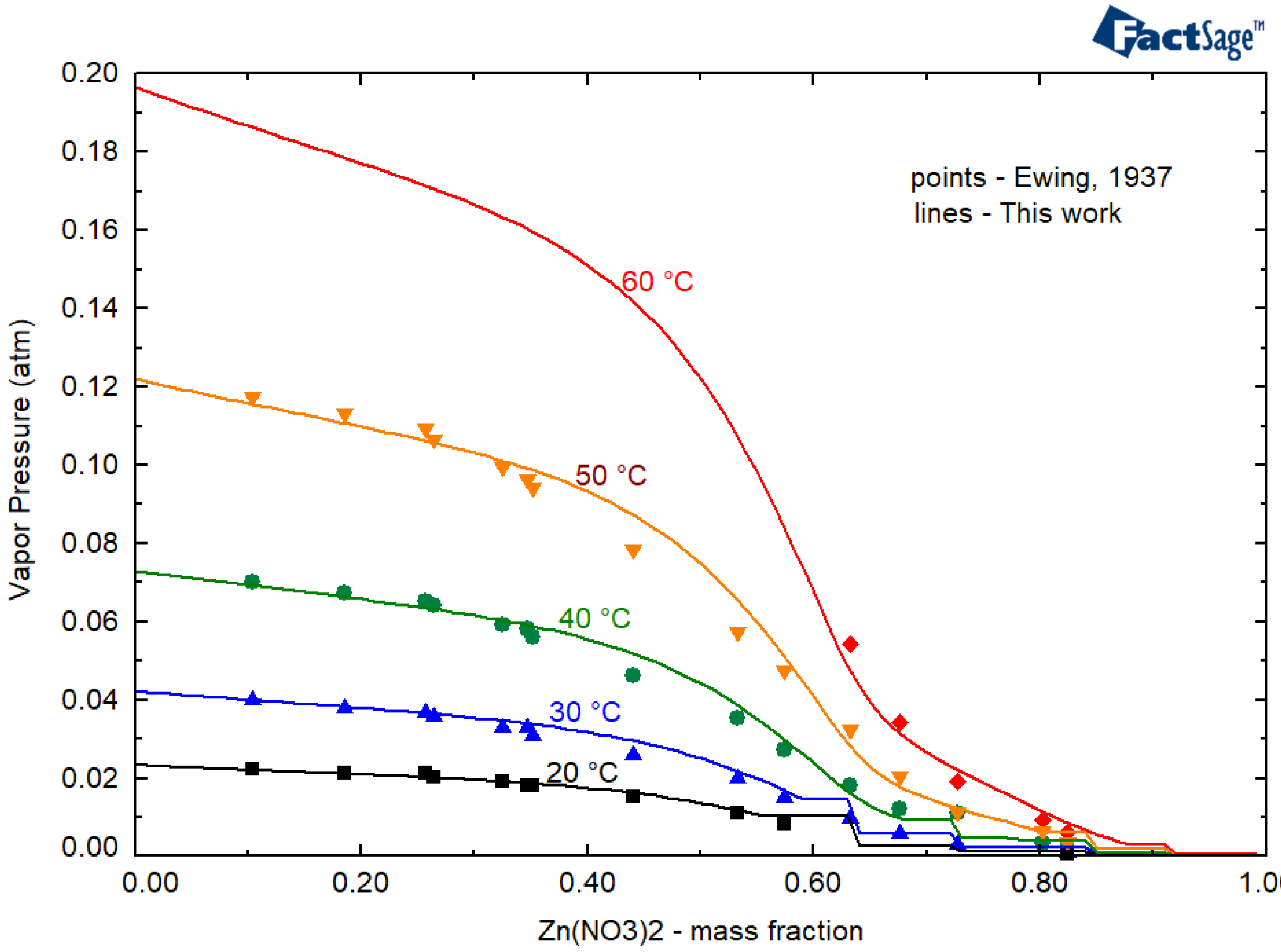
- $\Delta_r G°$
- $L^{0,1}(H_2O\text{-}Zn(NO_3)_2)$
- $L^{0,1}(H_2O\text{-Assoc.})$
- $L^{0,1}(\text{Assoc.-}Zn(NO_3)_2)$

} Optimized

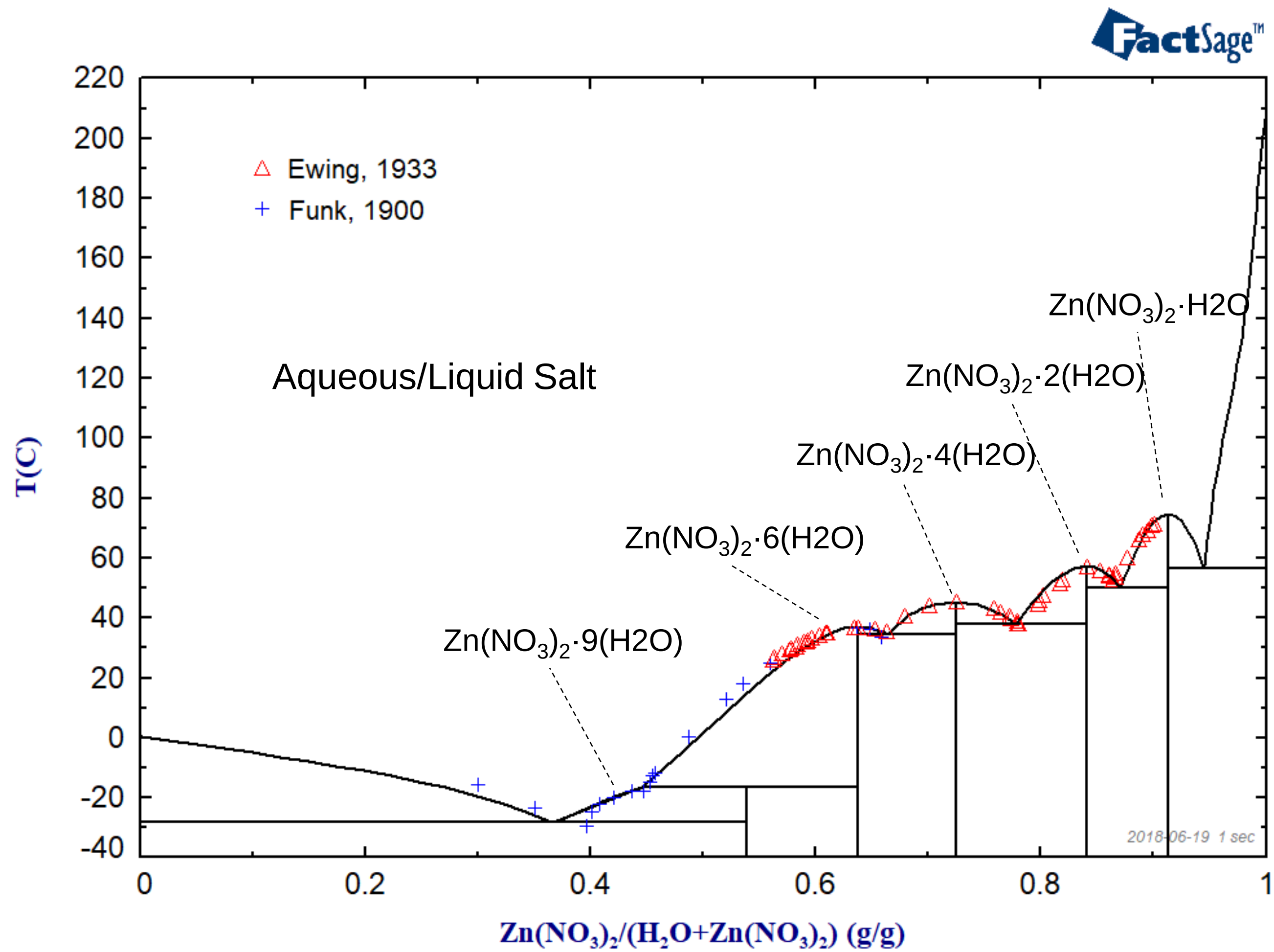
H_2O-$Zn(NO_3)_2$: Heat of Mixing at 25°C



H_2O-$Zn(NO_3)_2$: Vapor Pressure = f(x,T)



H_2O-$Zn(NO_3)_2$: Phase Diagram



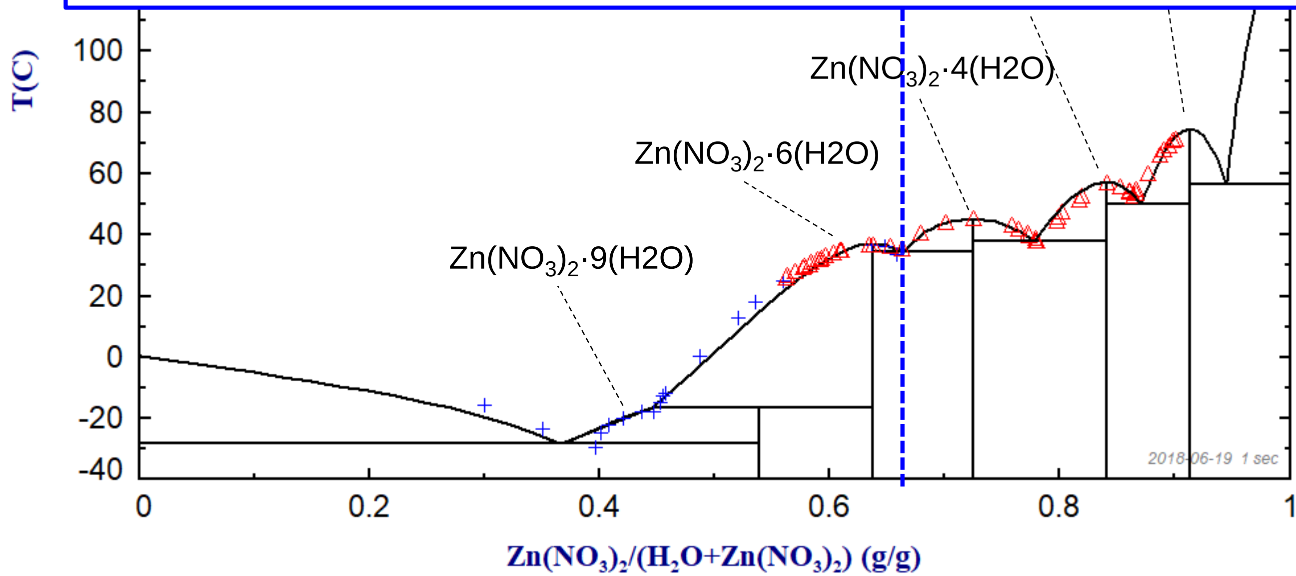
H_2O-$Zn(NO_3)_2$: Phase Diagram

<u>Eutectic at:</u>

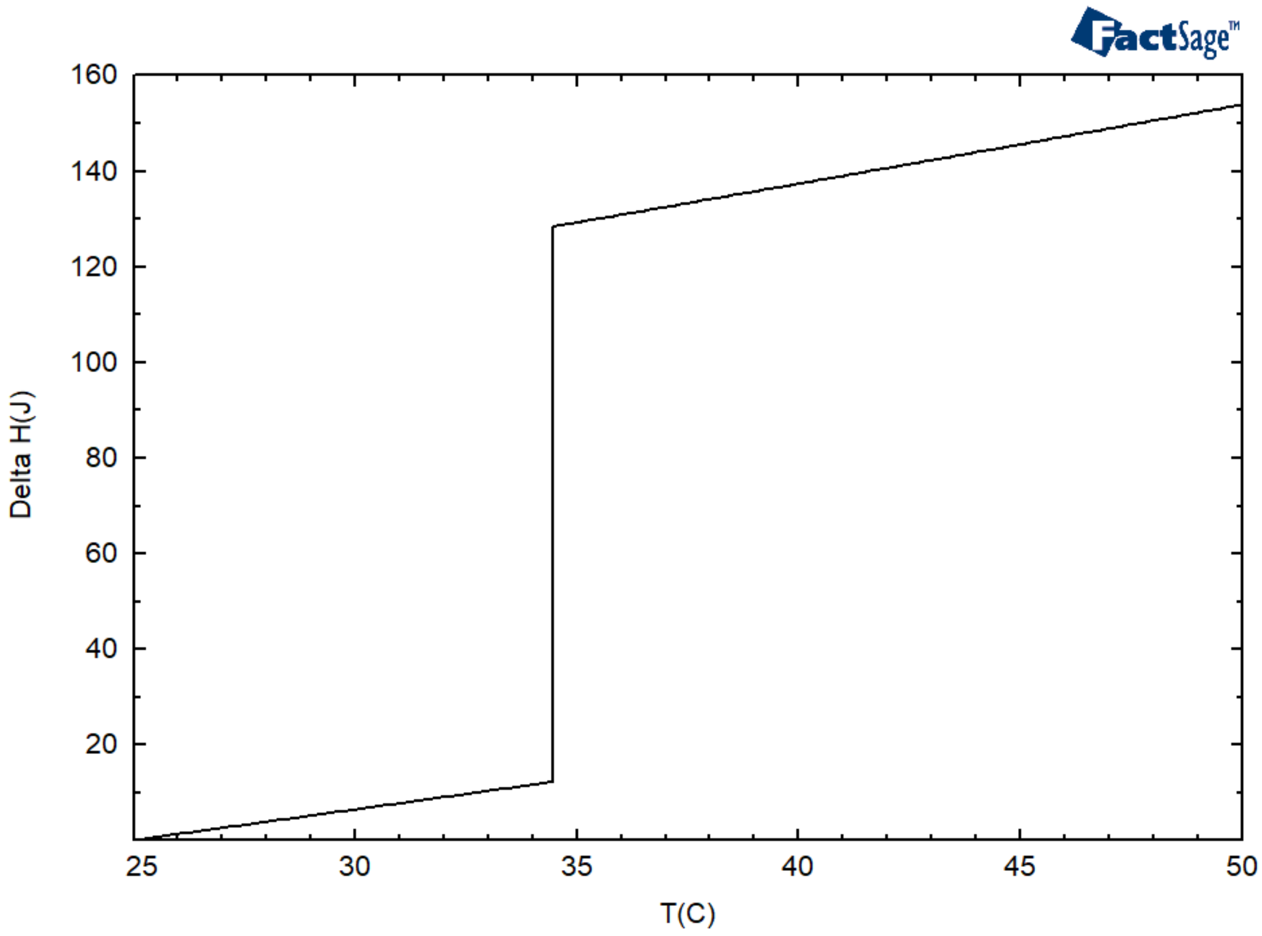
66.4 wt.% $Zn(NO_3)_2$

or

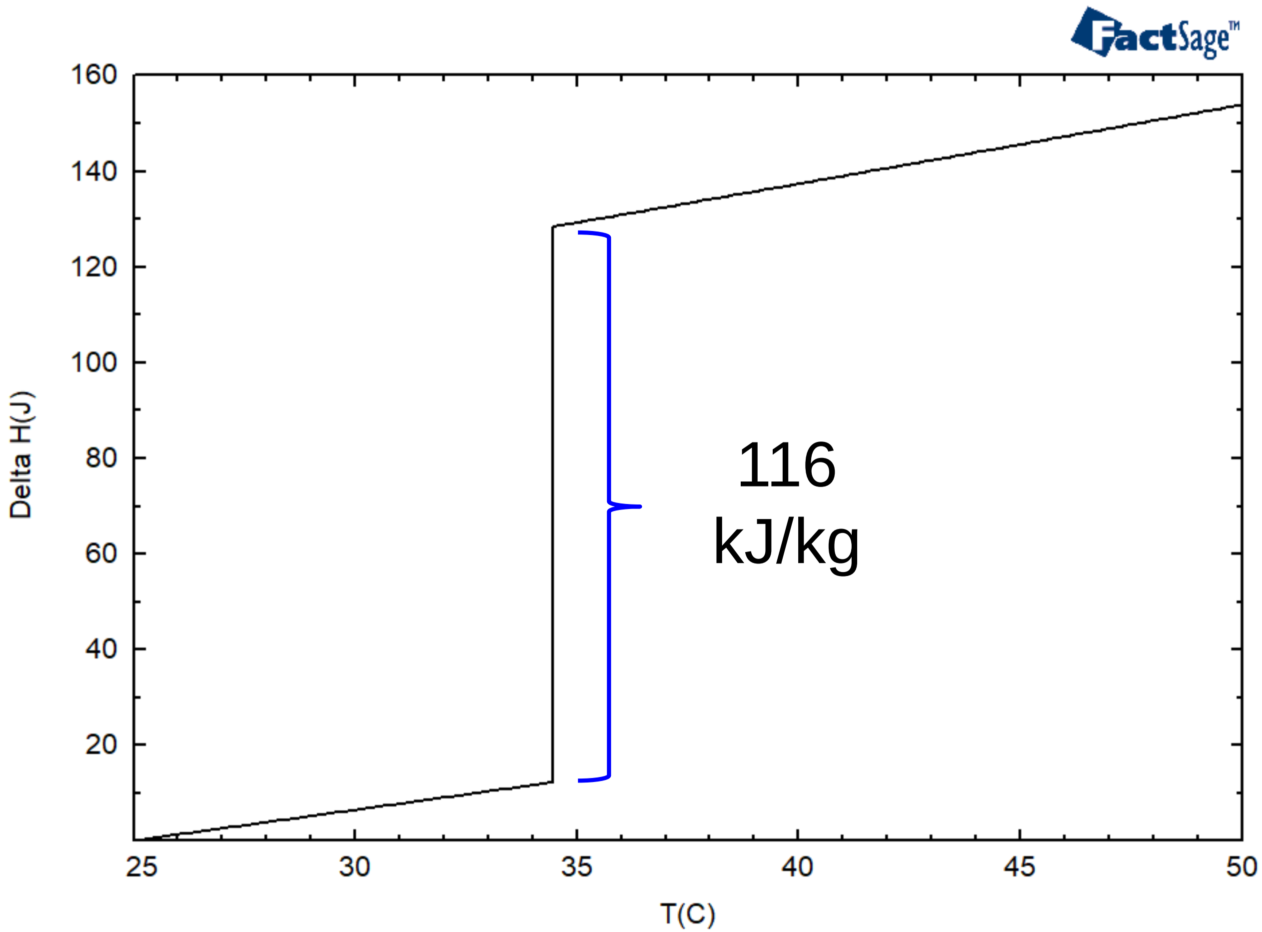
68.8 wt.% $Zn(NO_3)_2.6(H_2O)$ + **31.2 wt. %** $Zn(NO_3)_2.4(H_2O)$



H_T-H_{25C}: Eutectic at 66.4 wt.% $Zn(NO_3)_2$



H_T-H_{25C}: Eutectic at 66.4 wt.% $Zn(NO_3)_2$



Summary

- Aqueous Solution successfully described by the Non-Ideal Associate Species model, **without a Debye-Hückel type term**
- H_2O-$Zn(NO_3)_2$ 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