Challenges in developing predictive thermodynamic models for complex molten salts

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Lack of information for AkCl-AnCl$_3$ systems

- There is a lack of information on the mixing enthalpy ($\Delta_{mix}H$) and excess heat capacity (ΔC_p) for many actinides salt systems.
- A straight-forward methodology for predicting these values is of great value to CALPHAD.

Background and data mining

Davis' theory: $\Delta_{mix}H$ is described as a function of an interaction parameter λ^M that varies linearly with respect to a size parameter δ_{12} at constant temperature, composition and pressure.

$$\lambda^{M} = \frac{\Delta_{mix}H}{x_{AkCl}x_{MCl_3}} \qquad \delta_{12} = \frac{\left(r_{Ak}^{+} + r_{Cl}^{-}\right) - \left(r_{M}^{3+} + r_{Cl}^{-}\right)}{\left(r_{Ak}^{+} + r_{Cl}^{-}\right) \cdot \left(r_{M}^{3+} + r_{Cl}^{-}\right)}$$

where r_{Ak}^{+}, r_{M}^{3+} and r_{Cl}^{-} are the ionic radii of the alkali, lanthanide/actinide, and chlorine atom, respectively, coordination VI from compendium of Shannon.

Data mining of $\Delta_{mix}H$: 48 sets of data have been used to construct our analysis:

- La^{3+} (1.032 Å) to Yb^{3+} (0.868 Å)
- No data for AkCl-PuCl$_3$, and LiCl/RbCl/CsCl-UCl$_3$.
- CeCl$_3$–family offer a very good example of the behavior of AkCl-An/LnCl$_3$ systems.

LiCl-systems (8)	
LaCl$_3$	1173
CeCl$_3$	1130
PrCl$_3$	1044
NdCl$_3$	1044
GdCl$_3$	1263
TbCl$_3$	1109
YCl$_3$	1143
TmCl$_3$	1130

NaCl-systems (16)	
LaCl$_3$	1173
LaCl$_3$	1153
UCl$_3$	1113
CeCl$_3$	1153
CeCl$_3$	1118
PrCl$_3$	1122
NdCl$_3$	1124
SmCl$_3$	1153
GdCl$_3$	1263
TbCl$_3$	1109
DyCl$_3$	1153
DyCl$_3$	1100
YCl$_3$	1143
ErCl$_3$	1153
TmCl$_3$	1130
YbCl$_3$	1153

KCl-systems (11)	
LaCl$_3$	1173
UCl$_3$	1113
CeCl$_3$	1118
PrCl$_3$	1122
NdCl$_3$	1065
GdCl$_3$	1263
TbCl$_3$	1109
DyCl$_3$	1070
YCl$_3$	1143
YCl$_3$	1053
TmCl$_3$	1130

RbCl-systems (7)	
LaCl$_3$	1173
CeCl$_3$	1118
NdCl$_3$	1122
GdCl$_3$	1263
TbCl$_3$	1175
YCl$_3$	1143
TmCl$_3$	1130

CsCl-systems (6)	
LaCl$_3$	1173
CeCl$_3$	1118
NdCl$_3$	1122
GdCl$_3$	1263
TbCl$_3$	1175
YCl$_3$	1148

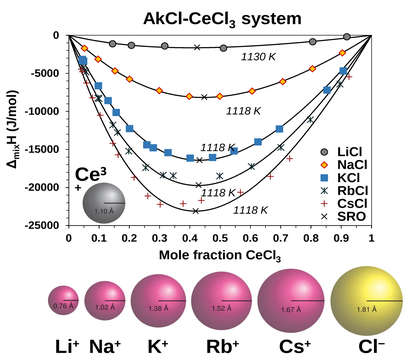

Fig. 1: The $\Delta_{mix}H$ values are negative and becomes more negative with increasing alkali radius.

- **Data mining of ΔC_p:** Only a few measurements were found (14 points) including chlorides and fluorides systems.

Data fitting and short-range ordering

Data fitting: Regression of the $\Delta_{mix}H$ functions using the Surrounded Ion Model.

$$\Delta_{mix}H = [(1-x)pq + xrs]x'(1-x')\left(f_1 + f_2x' + f_3x'^2\right)$$

$$x' = \frac{xrs}{[(1-x)pq + xrs]}$$

where $p = q = s = 1$, $r = 3$, and f_i are fitting coefficients.

Short-range ordering: A linear behavior of SRO vs δ_{12} allows reasonably accurate interpolation.

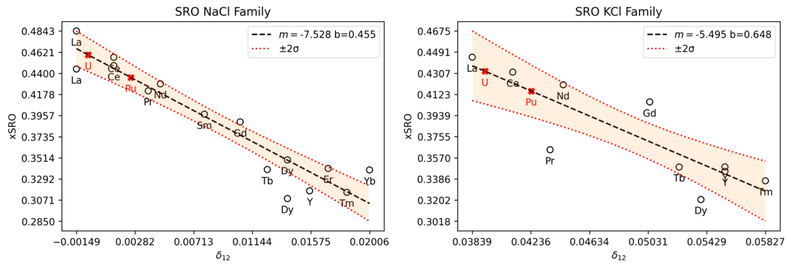

Fig. 2: Maximum SRO vs. δ_{12} plots with interpolated values for uranium and plutonium sodium and potassium chloride.

Correlation between $\Delta_{mix}H$ and ΔC_p: Redkin et al. proposed a linear relationship, which was improved by exponential equation proposed by Yingling et al.:

$$\Delta C_p = 1.795(-\Delta_{mix}H)^{0.616}$$

Validation of the method

NaCl-UCl$_3$ and NaCl-PuCl$_3$ are used to validate these methods for $\Delta_{mix}H$ and ΔC_p, respectively:

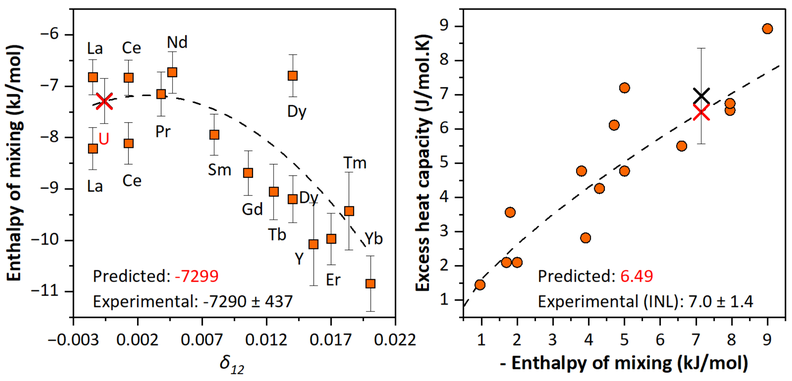

Fig. 3: $\Delta_{mix}H$ at the composition of maximum SRO for NaCl-containing systems and predicted ΔC_p for NaCl-PuCl$_3$ compared to Idaho National lab measurements.

Predictions for AkCl-An/LnCl$_3$ + CALPHAD

Predictions for unexplored systems: The methodology was applied to

- remaining AkCl-UCl$_3$ systems and AkCl-PuCl$_3$ systems
- 27 unexplored AkCl-LnCl$_3$ systems.

Thermodynamic assessment of NaCl- and KCl-PuCl$_3$: The methodology for determining $\Delta_{mix}H$ and ΔC_p are used in CALPHAD modeling of the AkCl-PuCl$_3$, AkCl-UCl$_3$ and AkCl-LnCl$_3$ (Ln = La, Ce, and Nd) systems, all available in the Molten Salt Thermal Properties Database – Thermochemical (*MSTDB-TC*).

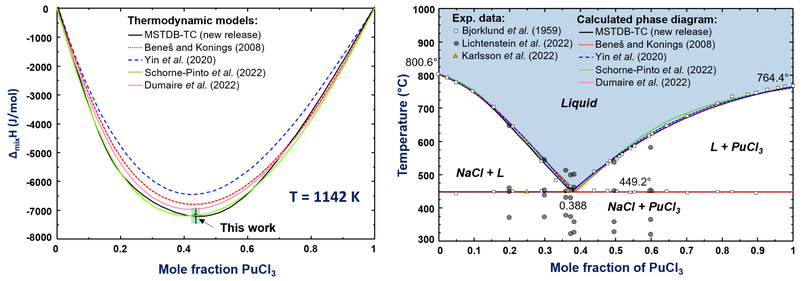

Fig. 4: Δ_{mix}H values of this work and those from literature, and computed phase diagram for the NaCl-PuCl$_3$ system of this work and literature.

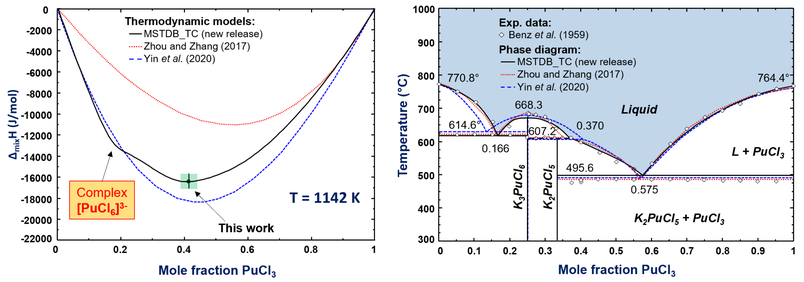

Fig. 5: Δ_{mix}H values of this work and those from literature, and computed phase

Acknowledgements

This research was supported by the Nuclear Energy Advanced Modeling and Simulation Program administered by Los Alamos National Laboratory, which is operated by Triad National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract number 89233218NCA000001.

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