U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Molten Salt Reactor PROGRAM

Generation of Molten Salt Thermochemical Properties at USC

Ted Besmann

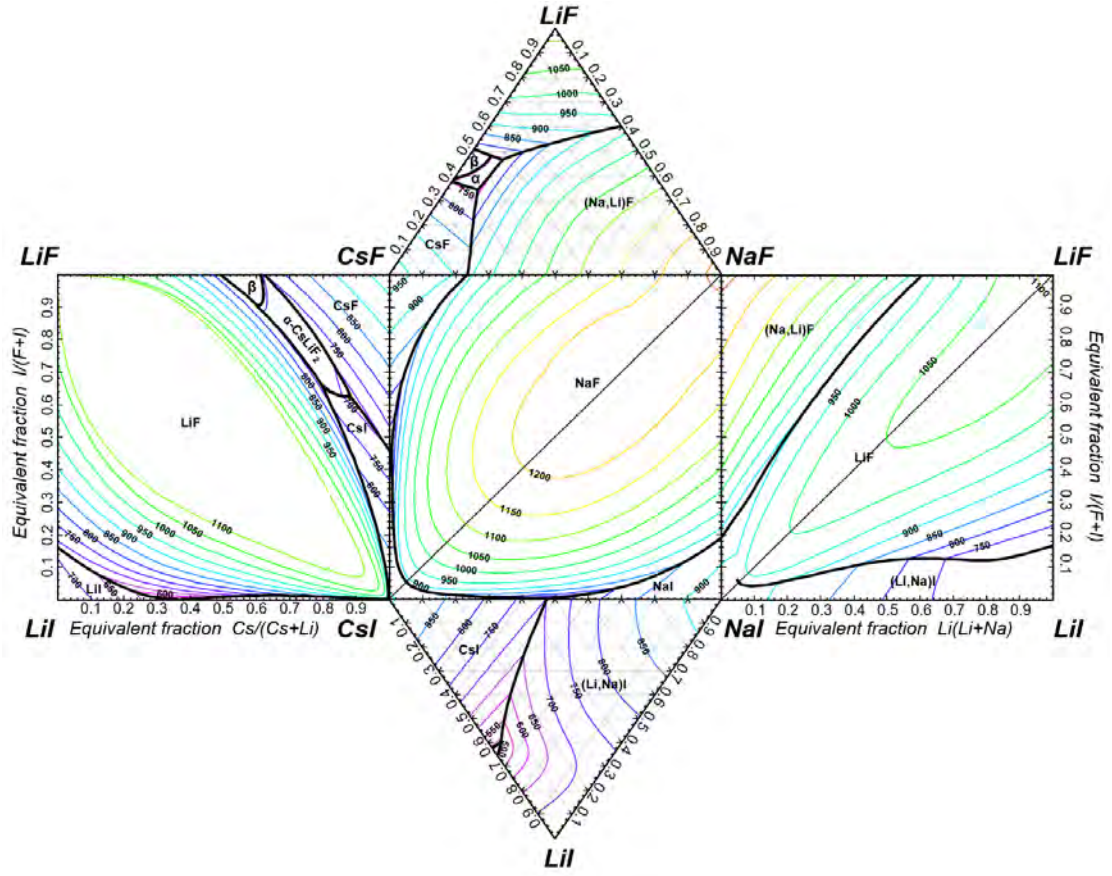
UNIVERSITY OF SOUTH CAROLINA

Annual MSR Campaign Review Meeting 16-18 April 2024

Contents

- Milestone/accomplishments in FY23 and FY24 to date
- Measurements and modeling for thermochemical values
- Reevaluation of FLiNaK and FLiBe systems
- Optmization of lanthanide-containing fluorides
  - LiF-NaF-(LaF_3, CeF_3, PuF_3)
- Optimization of fuel systems
  - NaCl-UCl_3-$PuCl_3$
  - LiF-BeF_2-ZrF_4-UF_4
- Modeling of iodine-containing reciprocal salt systems
  - Na, K, Cs, Mg | Cl, I
  - Li, Na, K, Cs, | F, I
- Applications
- Proposed/current FY24 efforts and data needed from program activities beyond those at USC

Computed liquidus projection for reciprocal salts Li Na Cs | F I



Milestone/Accomplishments

FY23 L4 Milestone: *Complete addition of $MgCl_2$ to NaCl and/or KCl with $UCl_{3,4}$ and reciprocal salts with iodine*. 7/31/2023

<u>Summary of FY23 and FY24 to-date accomplishments</u>

- Release of MSTDB-TC Versions 3.0 and 3.1
  - 74 iodine-containing systems
  - Inclusion of base salt ZrF_4 component systems
  - Addition of important fission products
    - SrF_2, BaF_2, YF_3, PrF_3, $LaCl_3$, $NdCl_3$, $ZrCl_4$
    - Mo, Ru, Rh, Tc, and Pd alloys and intermetallic compounds from direct incorporation of the models of Kaye et al.
    - He, Ne, Ar, Kr, and Xe, although absent any models for solubility in salt
  - Expansion of CsF-containing systems: CsF-ZrF_4, CsF-BeF_2, and LiF-CsF-BeF_2
  - Expansion of $PuCl_3$-containing systems: $PuCl_3$ with LiCl, NaCl, KCl, $MgCl_2$, UCl_3 plus higher-order systems
  - Inclusion of relevant heterocomplex vapor species
- Modeled NiF_2, FeF_2, CeF_3, PuF_3, and LaF_3 solubilities in FLiBe (Ni and Fe efforts performed under a NEUP)
- Revision of FLiNaK and FLiBe systems, and modeling of FLiBe-UF_4
- Modeled LiF-NaF-UF_4 and KF-NaF-UF_4 pseudo-ternary systems
- Modeled K,Mg|Cl,I and Mg,Na|Cl,I reciprocal systems and accompanying CsCl-$MgCl_2$ and CsCl-NaCl pseudo-binaries
- Reevaluated the LiF-NaF-(LaF_3, CeF_3, PuF_3) pseudo-ternary systems

Publications & Workshop

Workshop

Training/Workshop for the
Molten Salt Thermal Properties Databases
Hosted by the University of South Carolina
Virtual, April 25, 2023
Organizers Dianne Ezell (ORNL) and Ted Besmann (USC)

Publications

Applications of Thermochemical Modeling in Molten Salt Reactors, T. M. Besmann, J. Schorne-Pinto, M. Aziziha, A. M. Mofrad, R. E. Booth, J. A. Yingling, J. Paz Soldan Palma, C. M. Dixon, J. A. Wilson, D. Hartanto, Materials 17(2) (2024) 495.

Thermal Property Modeling and Assessment of the Physical Properties of FLiNaK, J. Schorne-Pinto, M. Aziziha, H. B. Tisdale, A. M. Mofrad, A. Birri, M. Christian, J. C. Ard, Johnathan, R. E. Booth; J. A. Yingling, J. Paz Soldan Palma, C. M. Dixon, H.-C. zur Loye, T. M. Besmann. ACS Applied Energy Materials, accepted.

Thermodynamic Reassessment of CsF with FLiNaK, C. M. Dixon, J. A. Yingling, J. Schorne-Pinto, M. Aziziha, and T. M. Besmann, J. Moll. Liq. Accepted.

A Comprehensive Thermochemical Study of LiF, NaF, and KF Alkali Fluorides: How Accurate Current Liquid and Gas Thermodynamic Functions?, J. Schorne-Pinto, M. Aziziha, H. B. Tisdale, M. Christian, J. C. Ard, R. E. Booth, K. R. Foster, J. A. Yingling, C. M. Dixon, A. M. Mofrad, H.-C. zur Loye and T. M. Besmann, J. of Physical and Chemical Reference Data, final revisions

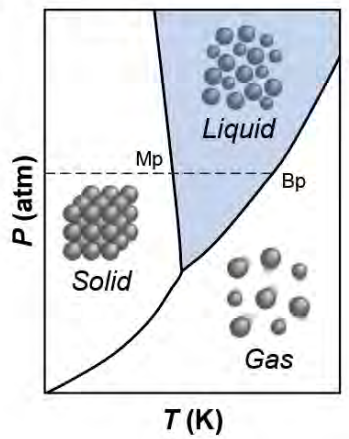
MSTDB-TC Development Based on the CALPHAD Method

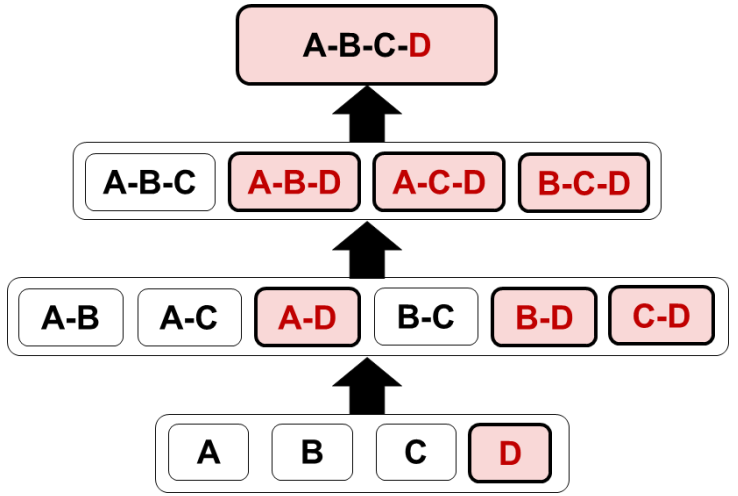
Molten Salt Thermal Properties Database −Thermochemical (*MSTDB-TC*) is a self-consistent **thermodynamic database designed for use by the molten salt reactor community**

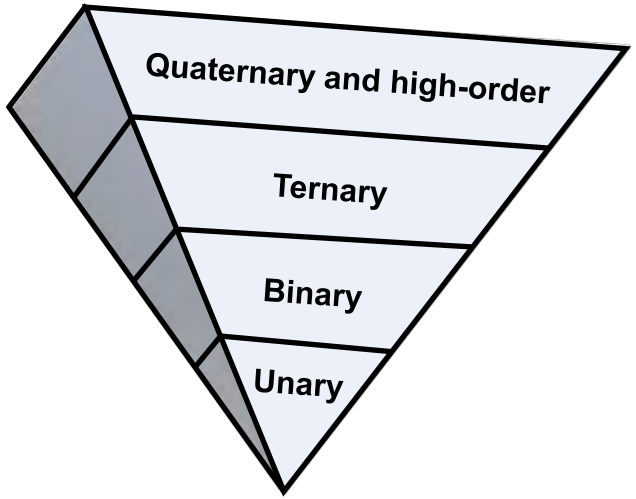
- CALPHAD method - based on minimizing the total Gibbs energy of the system
- Careful assessments to assure the quality of high-order systems
- Exhaustive literature review
- Critical evaluation of experimental data
- Measurements are made to fill knowledge gaps

Evaluated thermodynamic properties

- $\Delta_f H^o$ (cr, 298.15 K)
- S^0(cr, 298.15 K)
- $C_p(T)$
- T_{trans}
- T_{fus}
- ΔH_{fus}
- $T_{boiling}$
- ΔH_{vap}
- ΔS_{vap}







CALPHAD Inverted Pyramid

Radiological Facilities at USC (U and Limited Pu) Supporting MSTDB-TC Development

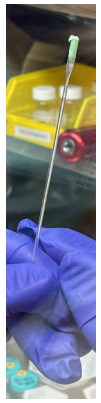
Two 750 sq. ft. laboratories

- Gloveboxes

> 40 salts (chlorides, fluorides and iodides)
Purification furnace system inside glovebox

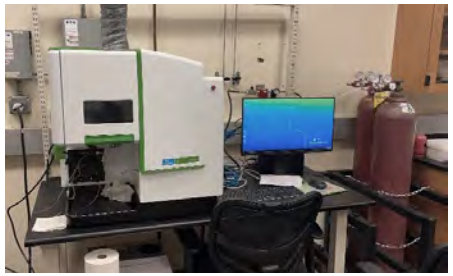
- XRD (+3 other units)

Rigaku Smartlab XRD (RT-1100 °C)



- Chemical analysis

Chemical analysis by ICP-OES



Elementrac for O_2 and H_2

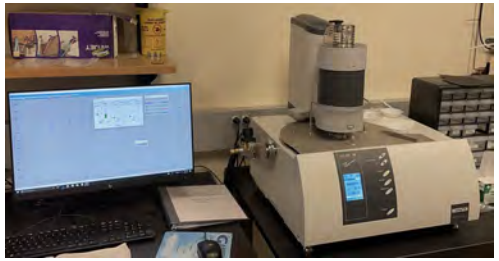
- Furnaces

2xMuffle (RT-1100 °C)

Tube furnace (RT-1700 °C)

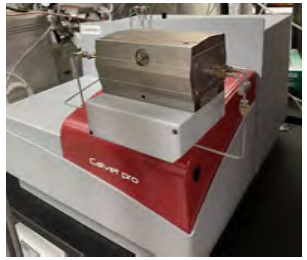
- Calorimeters

DSC 404 F3 Pegasus® - Netzsch



STA 449 Jupiter® - Netzsch

Calvet Pro - Setaram



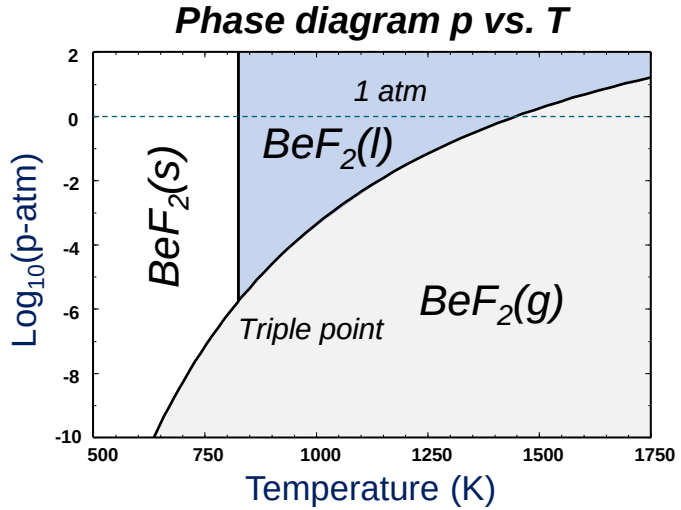
Melting points (±3 K), enthalpy of fusion (±3% for HF DSC, ± 1% Calvet), C_p (2% solid and 3% liquid using the Calvet)

Thermodynamic Descriptions for Pure Salts and Mixtures

Phases with fixed composition (**stoichiometric**):

$$\Delta G_i^\circ(T) = \Delta_f H_{298.15}^\circ(i) + \int_{298.15}^{T} C_{P_i}^\circ(T)\,dT - T\left(S_{298.15}^\circ(i) + \int_{298.15}^{T} \frac{C_{P_i}^\circ(T)}{T}\,dT\right)$$

- $\Delta_f H_{298.15}^\circ(i)$ is the standard enthalpy of formation
- $S_{298.15}^\circ(i)$ is the standard entropy
- $C_{P_i}^\circ(T)$ is the isobaric heat capacity



Phases with variable composition (**solutions**)

Derivatives of Gibbs energy
enthalpy, entropy, heat capacity

Phase equilibrium data
phase boundaries

$$\Delta G_m^\circ(T) = \sum_{i=1}^{n} x_i \Delta G_i^\circ(T) + RT\sum_{i=1}^{n} x_i ln(x_i) + \Delta G_m^{xs}(T)$$

Reference | Ideal | Excess

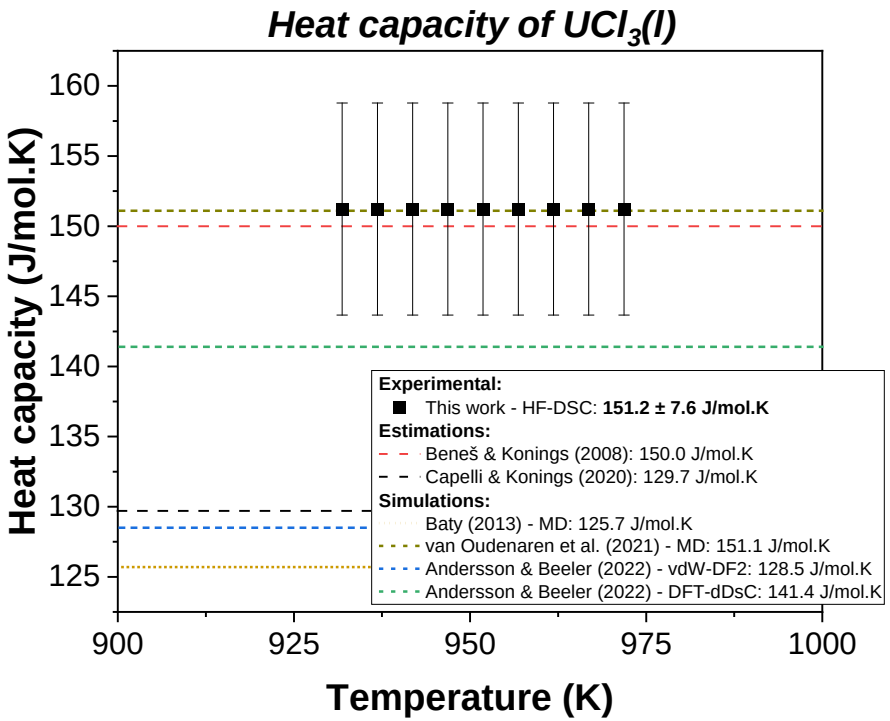
Adjusted to obtain the best representation of observed behavior

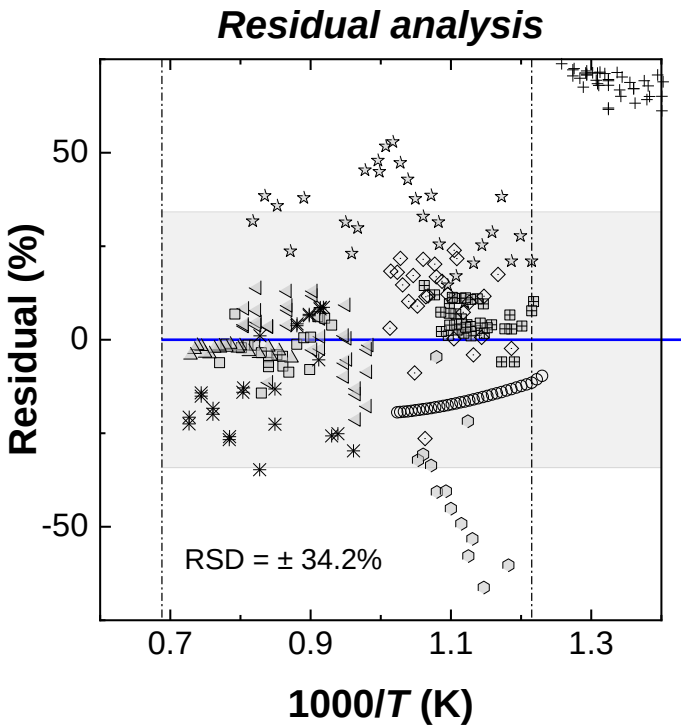
Recent Efforts on Verifying/Improving Unary (Endmember) Salt Descriptions

Pure salts → Binary → Ternary → Multicomponent

Evaluated thermodynamic properties:

- $\Delta_f H^0$ (cr, 298.15 K)
  - Dissolution calorimetry (better)
  - emf (good-better)
  - DFT (good)
- S^0 (cr, 298.15 K)
  - Adiabatic calorimetry (better)
  - PPMS (good-better)
  - emf (good)
- C_p (T)
  - HF-DSC (poor-good)
  - Calvet DSC (better)
  - Drop (good)
  - MD (poor-good)
  - AIMD (poor-good)
- T_{fus}
  - DSC/DTA (good)
  - emf (better)
- Vapor pressure
  - Transpiration (good)
  - Knudsen effusion (better)

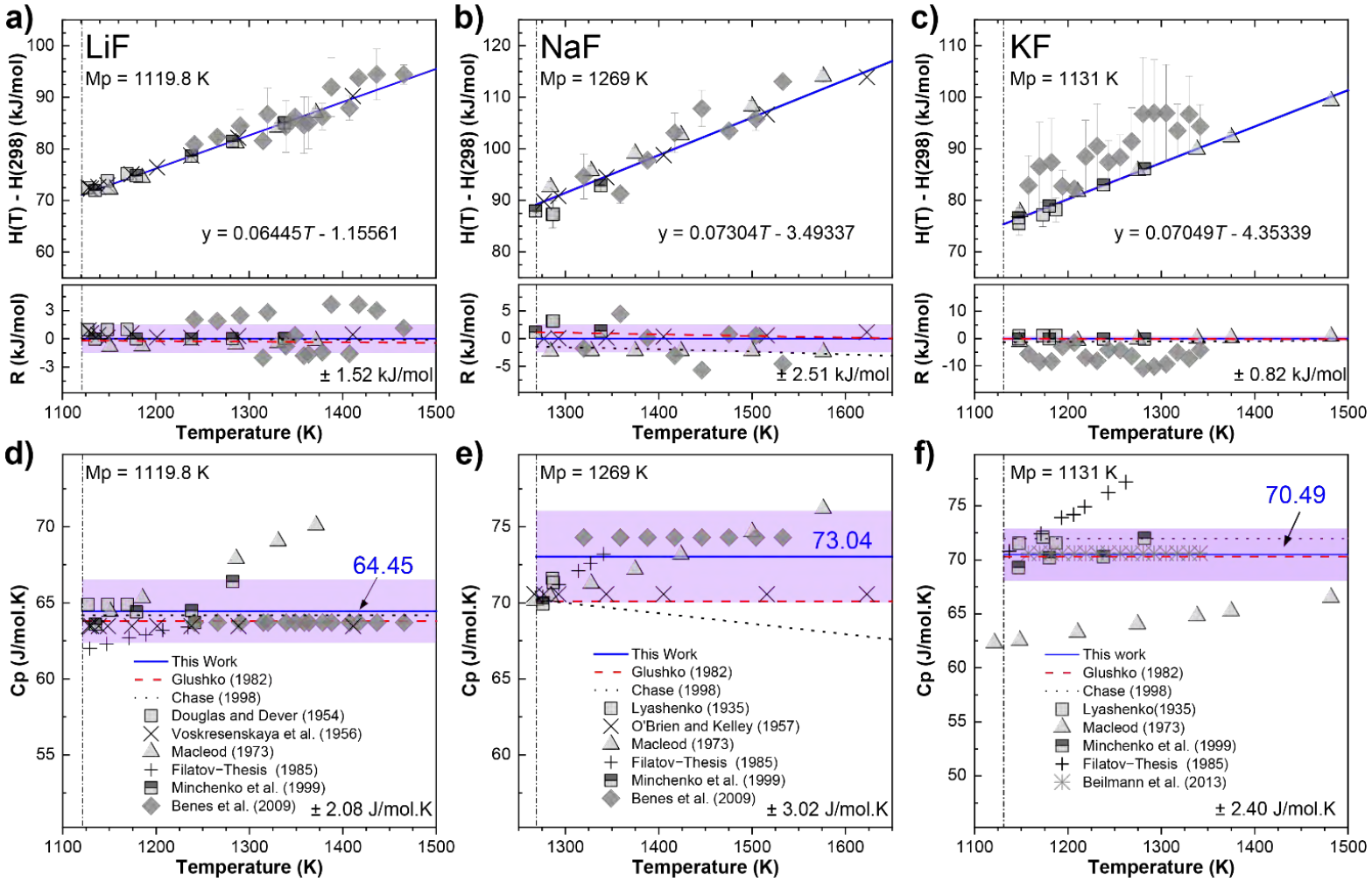




Evaluation of Thermal Properties for Alkali Fluorides

- Concern over the sometime wide range of reported values for alkali fluorides prompted a review of unary system values
- Independent sets of values were generated in this effort and together with reported information yielded recommended values
- Values for KF were sufficiently different than previously assumed that all KF-containing systems in MSTDB-TC were re-optimized,

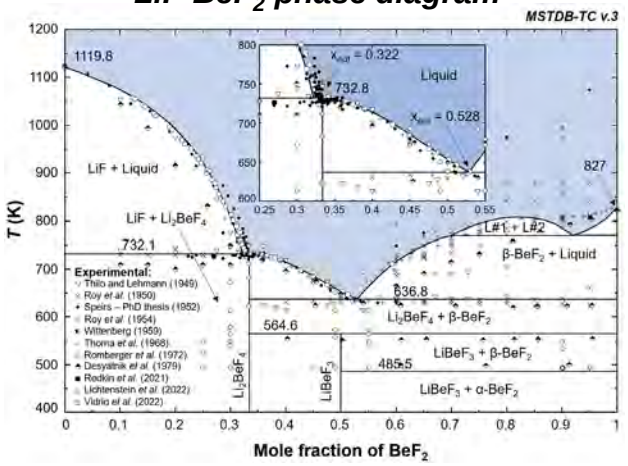
Reported and computed enthalpy increment and residuals and resultant Cp values



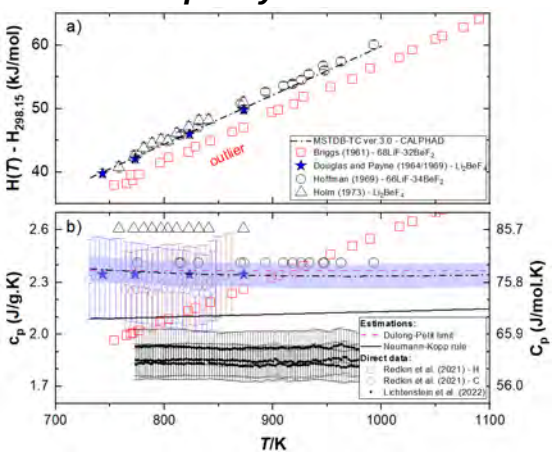
New FLiBe and FLiNaK System Optimizations

- Issues were seen in reported values for FLiBe
  - Heat capacity varies widely and required a critical assessment to resolve
  - Uncertainty in the melt temperature for BeF_2 remain and need to be experimentally resolved
- Importance of heterocomplex vapor species for FLiBe systems was revealed
- Measured and computed thermal properties for FLiNaK also exhibit a wide range of values and thus required measurements at USC to help resolve

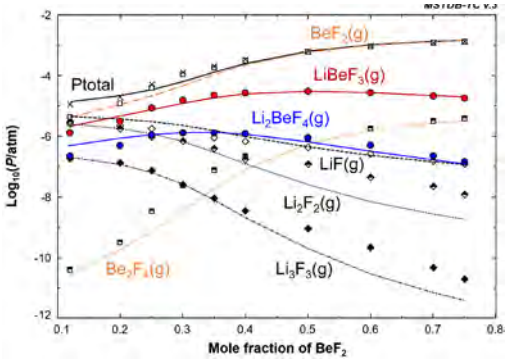
LiF-BeF_2 phase diagram



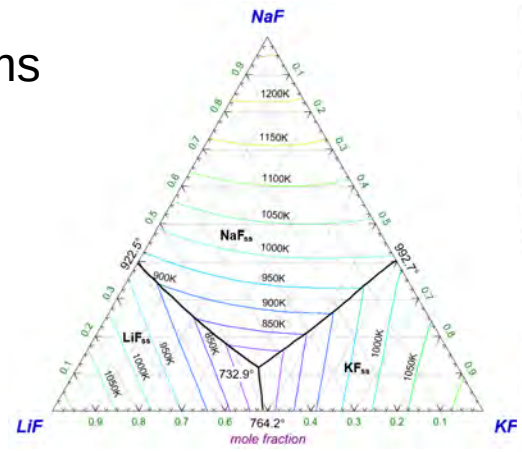
Heat capacity evaluation

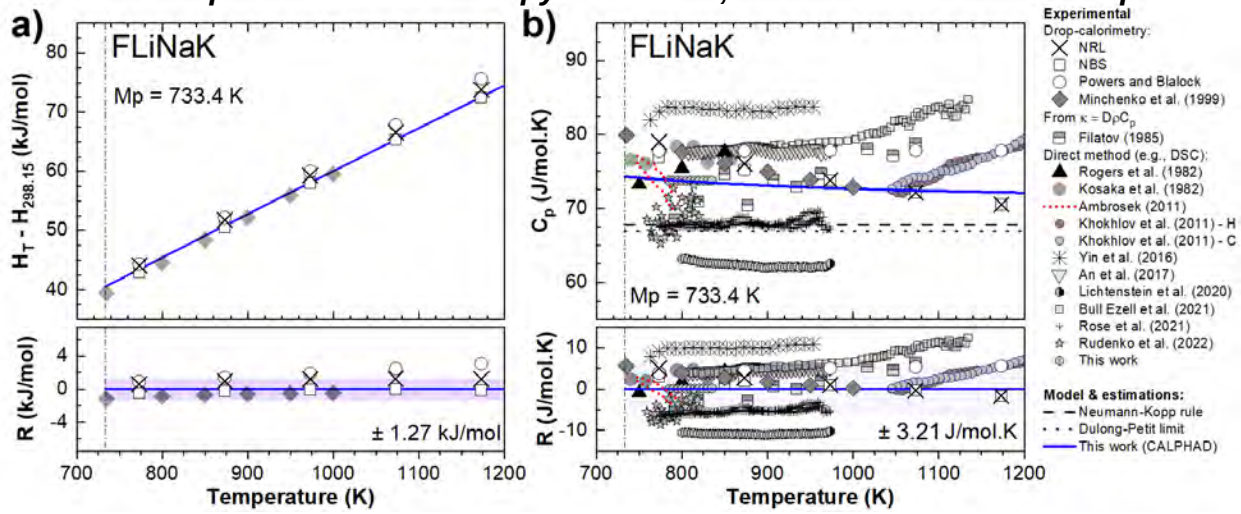


Heterocomplex of vapor species



Reported and computed FLiNaK enthalpy increment, residuals and resultant Cp values

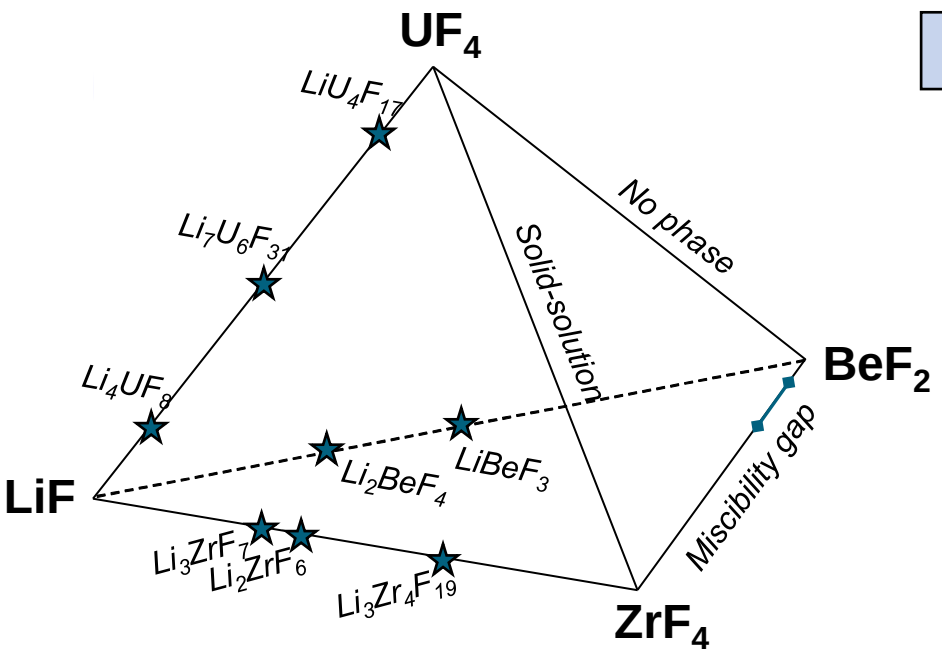




Thermochemical Models for FLiBe-ZrF_4-UF_4 (MSRE Fuel)

Pure salts → Binary → Ternary → Multicomponent

Base salt systems



Optimized

LiF-BeF_2-ZrF_4-UF_4

LiF-BeF_2-ZrF_4 | LiF-BeF_2-UF_4 | LiF-UF_4-ZrF_4 | BeF_2-UF_4-ZrF_4

LiF-BeF_2 | LiF-ZrF_4 | LiF-UF_4 | BeF_2-ZrF_4 | BeF_2-UF_4 | ZrF_4-UF_4

*Thermophysical properties of the MSRE fuel salt**

	ORNL reports	**MSTDB-TC ver. 3.0**	**≠**
Melting point	722 K	717.6 K (93% melted) 743.6 K (100%)	**21.6 K**
Specific heat	2010 J/kg.K	1966 J/kg.K 1681 J/kg.K (NKR)	**-2.2%** **-16.4%**
Vapor pressure (1300 K)	0.013 atm (3.95ZrF_4) 0.018 atm (8.13ZrF_4)	0.016 atm	**+23%** **-11%**

**Schorne-Pinto – unpublished*

CsF-containing Systems Optimized With Fluoride Fuel Salt

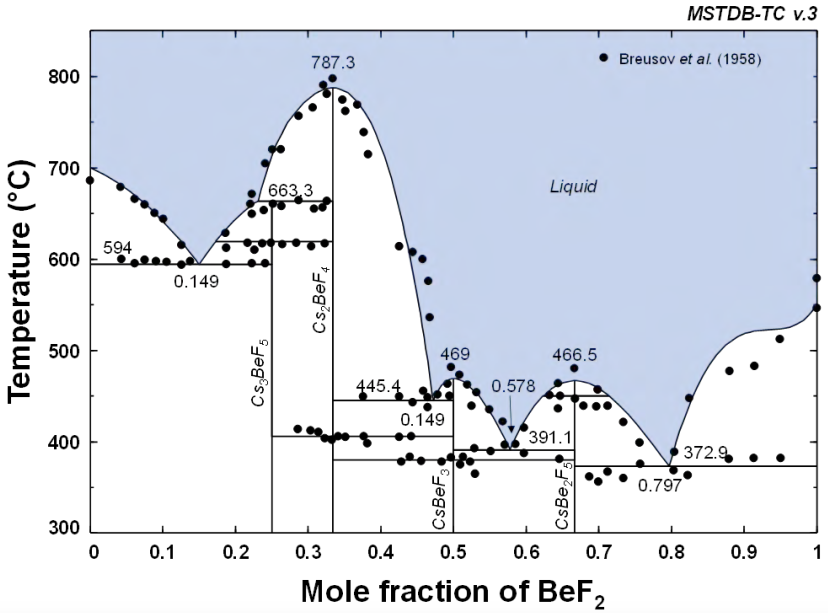
Pure salts → Binary → Ternary → Multicomponent

Efforts to include CsF

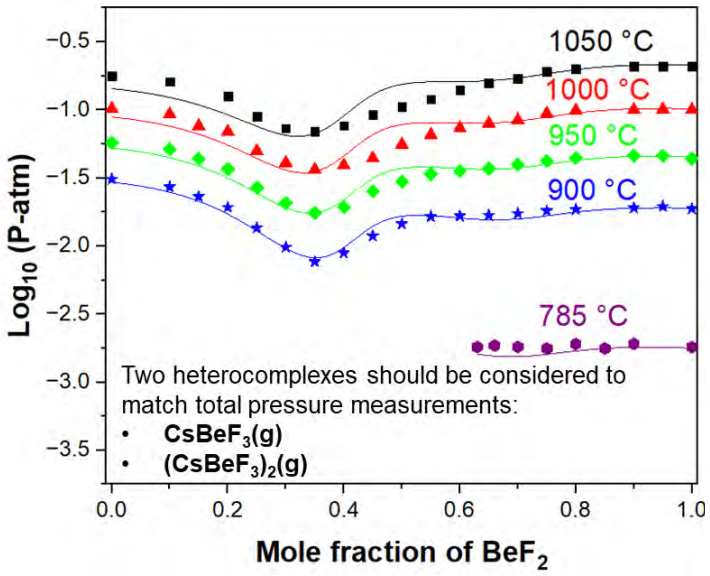
LiF-BeF_2-CsF …

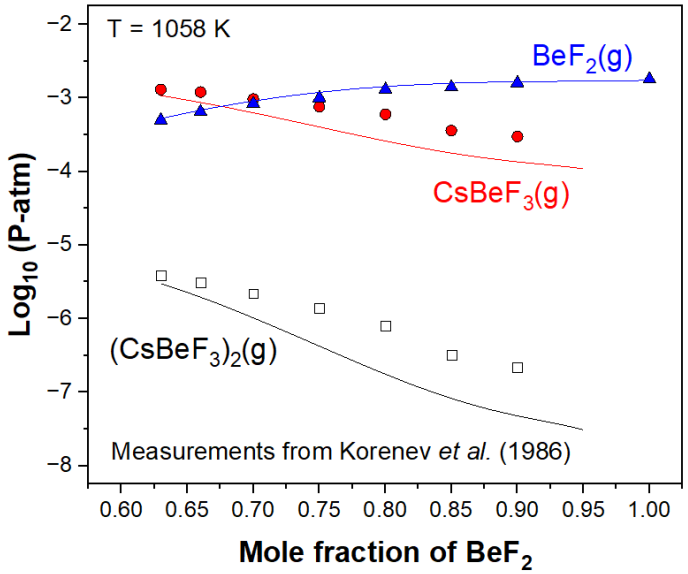
LiF-CsF | BeF_2-CsF | ZrF_4-CsF | UF_4-CsF

$CsF-BeF_2$ phase diagram



Total vapor pressure in the $CsF-BeF_2$ system*

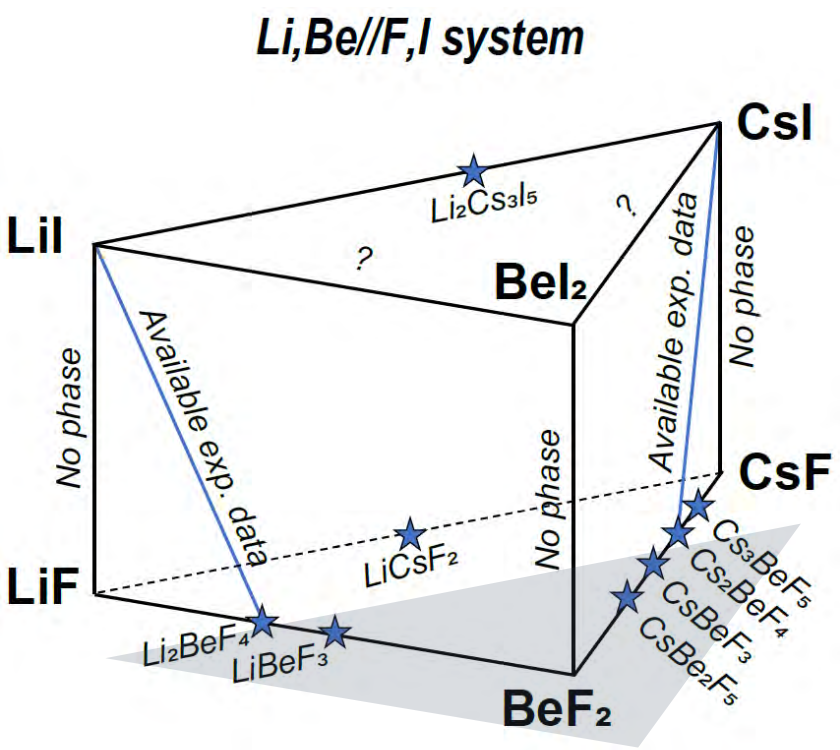


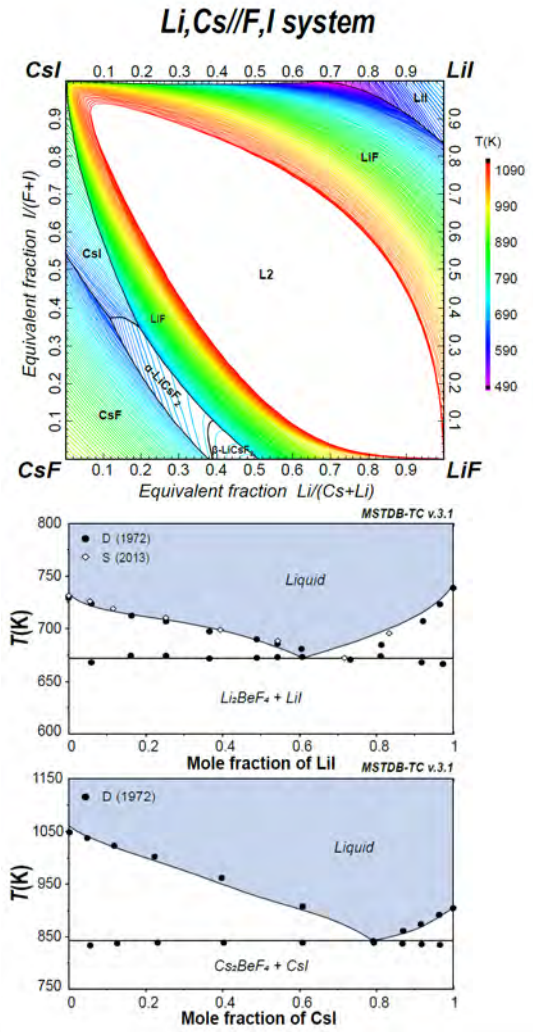


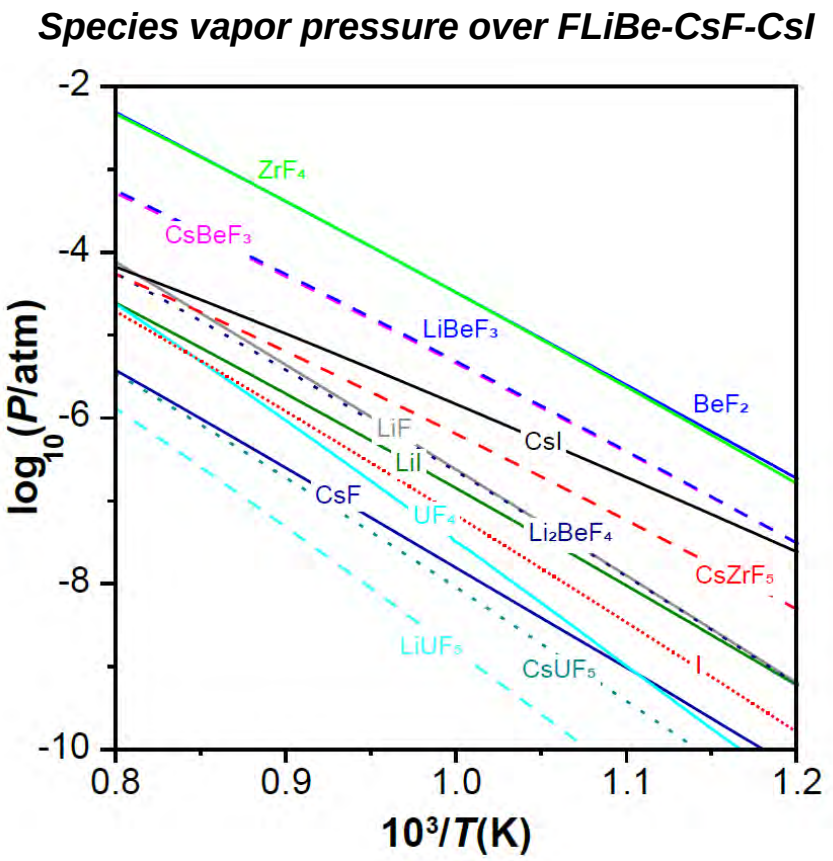
**Schorne-Pinto – unpublished*

Reciprocal Salt Models Necessary to Model Iodine Behavior in Fuel Salts

- Addressed to provide inputs for severe accident analysis



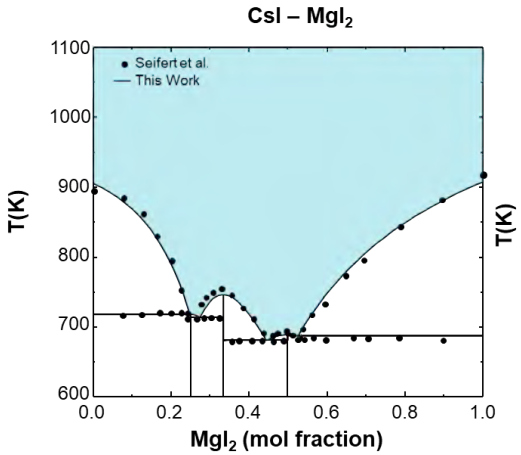


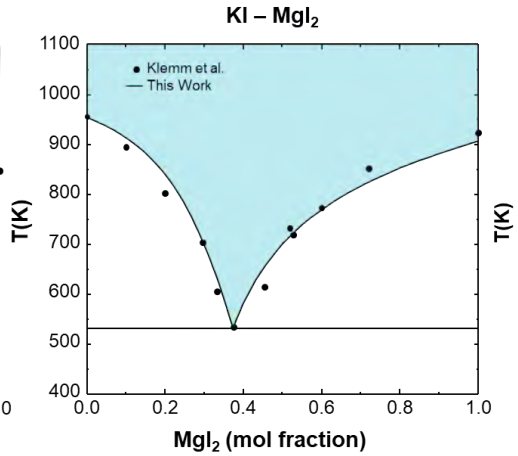


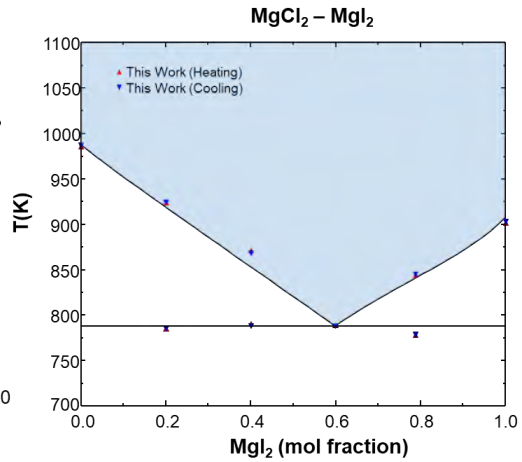
Individual Pseudo-Binary M | Cl, I (M=Na, K, Mg, Cs) Systems Required Novel Evaluation/Optimization

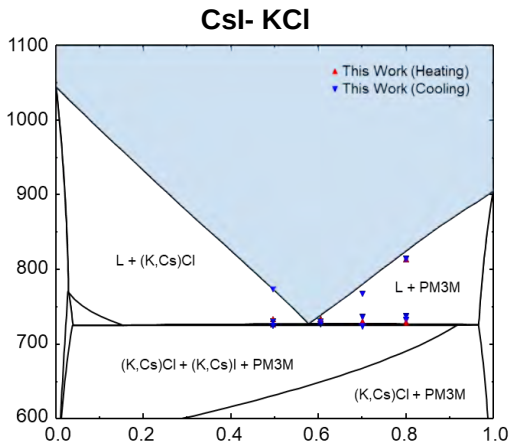
Evaluated systems

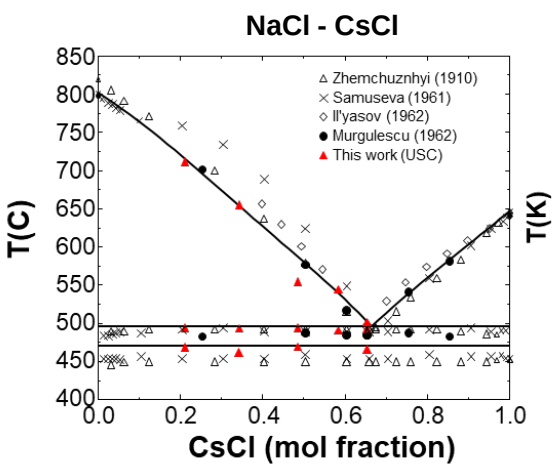
- NaCl-CsCl
- $MgCl_2$-CsCl
- MgI_2-$MgCl_2$
- NaI-MgI_2
- KI-MgI_2
- CsI-MgI_2
- CsI-KCl
- CsI-$MgCl_2$

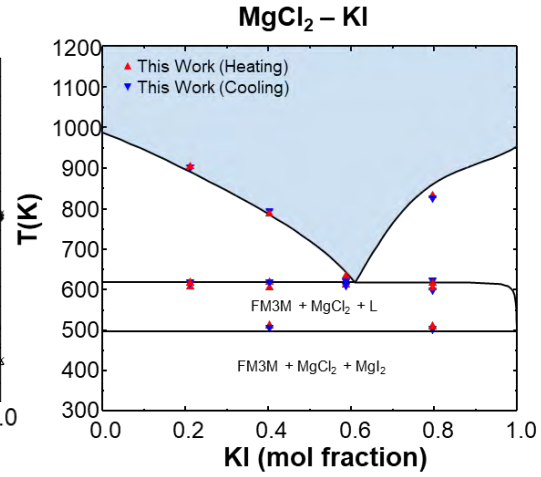


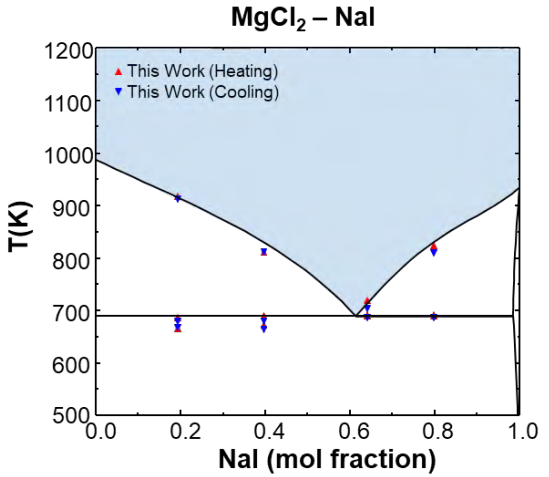


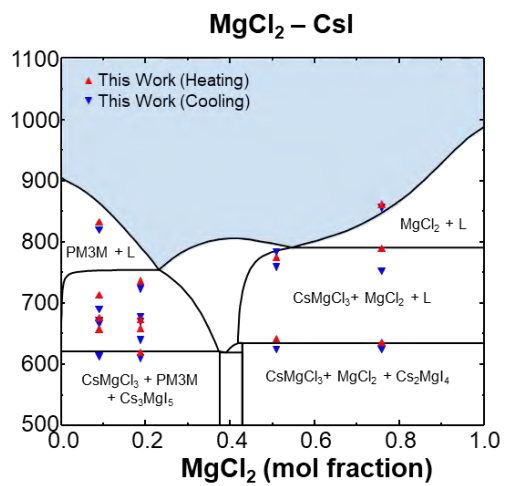












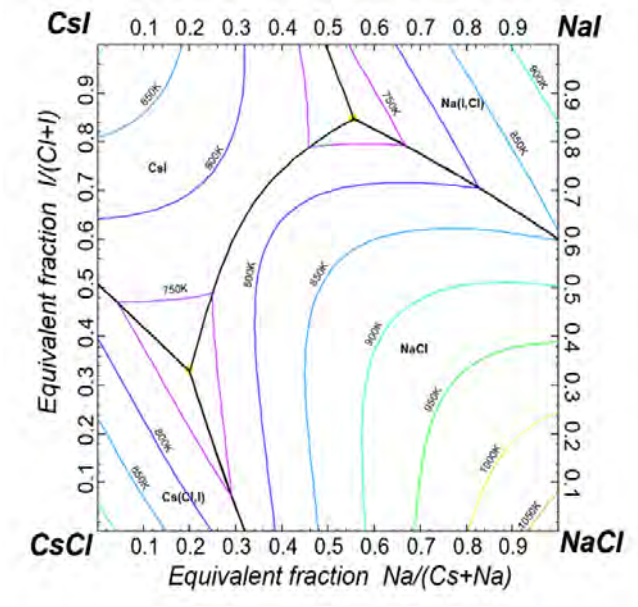
Resultant Optimized Reciprocal Salts & Higher Order Systems Can Now Represent Key Systems

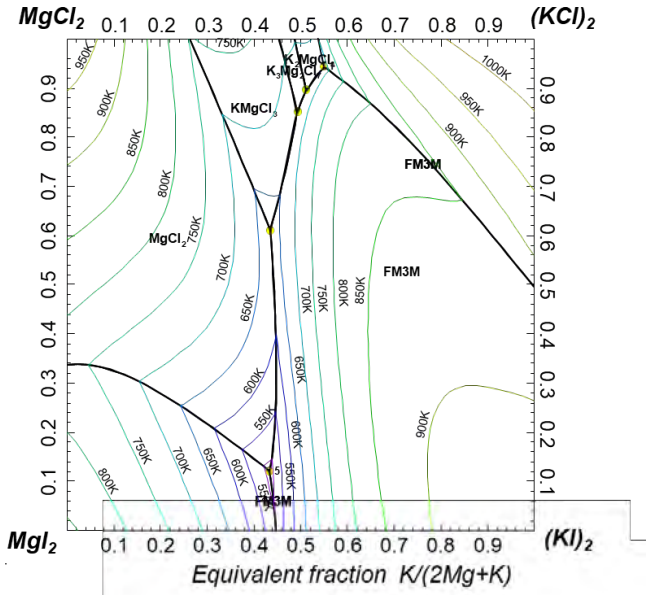
Reciprocal systems :

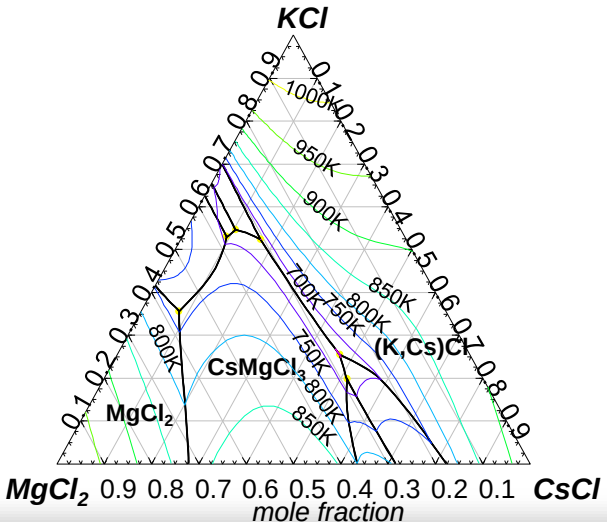
- K, Cs | Cl, I
- Na, Mg | Cl, I
- K, Mg | Cl, I
- Cs, Mg | Cl, I
- Na, K | Cl, I
- Na, Cs | Cl, I

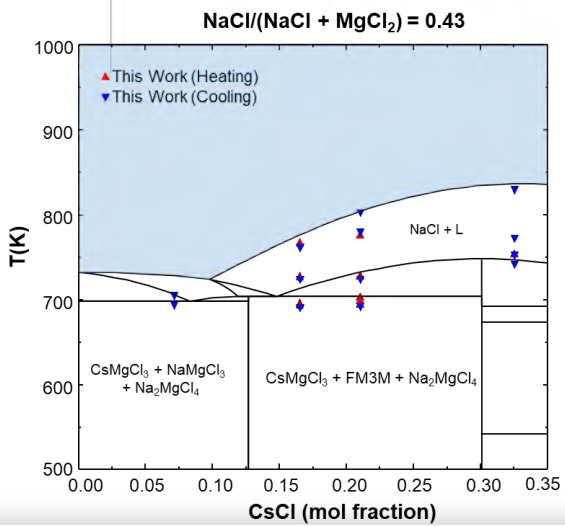
Higher order systems:

- NaCl-KCl-CsCl
- CsI-NaI-KI
- CsCl-NaCl-$MgCl_2$
- CsCl-KCl-$MgCl_2$
- NaI-KI-MgI_2
- CsI-NaI-MgI_2
- CsI-KI-MgI_2









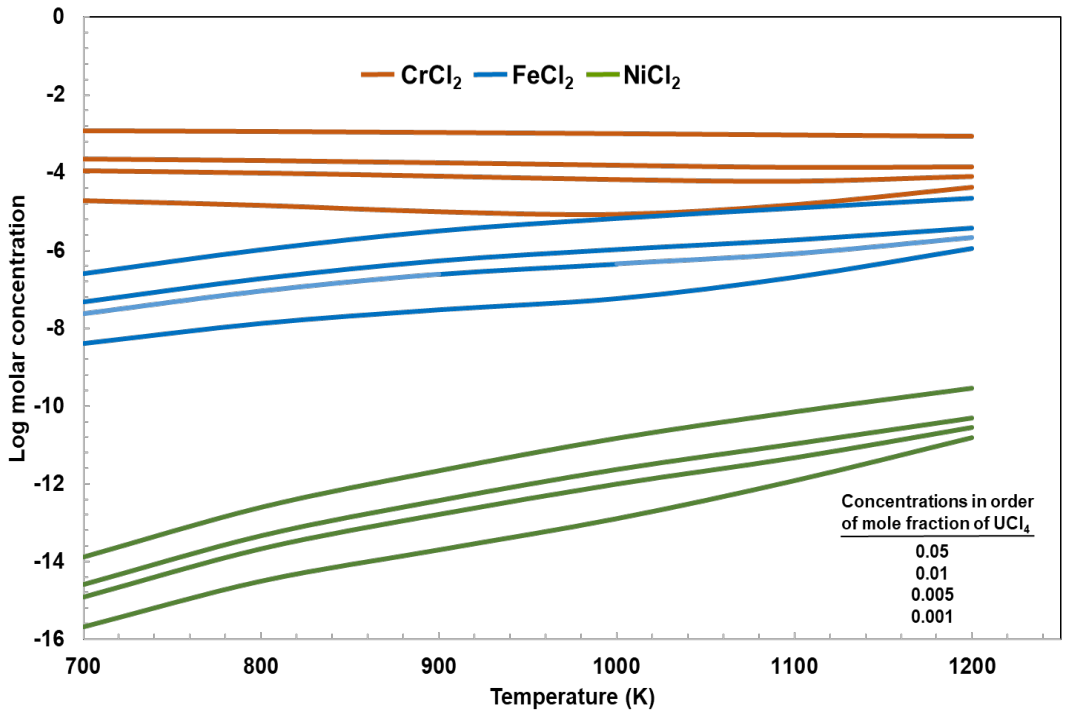
Examples of MSTDB-TC Utilization

- Under the NEAMS program efforts have initially coupled the codes Griffin/Pronghorn/Thermochimica/Mole for simulation of MSR behavior
  - Griffin and Pronghorn provide neutronics that allow depletion calculations supplying local elemental composition codes
  - Elemental composition used in Thermochimica which calls MSTDB-TC to calculate allows equilibrium state of salt
    - Speciation
    - Concentration
    - Halide potential
    - Phase precipitation
  - Mole code allows for mass accountancy/tracking of species in MSR fuel/coolant loop

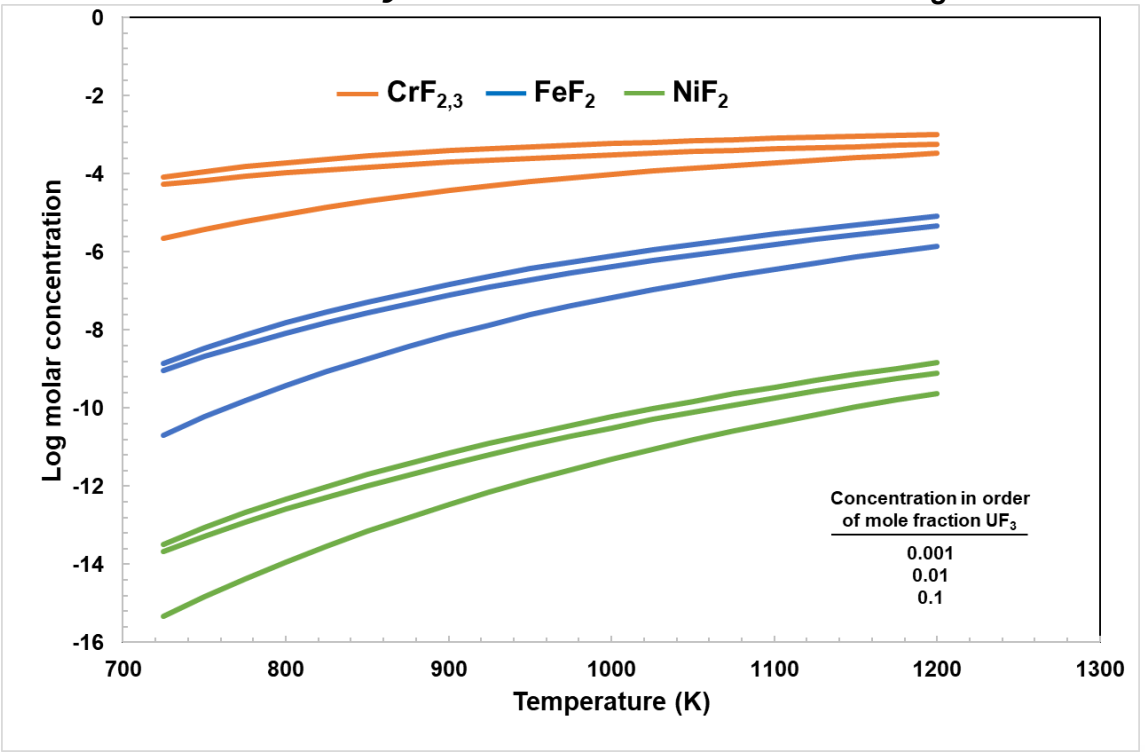
MSTDB-TC Library of Functions Can Contribute to Modeling of Corrosion

- Increasing halide potential ⇒ increased corrosion product concentration (unsurprising)
  - Increased UCl_4 content in UCl_3
  - Decreased UF_3 content in UF_4
- Little temperature dependence of critical Cr-halide concentration (observed in fluoride salt loop)

316SS* in high-KCl eutectic of KCl-$MgCl_2$-5 mol% UCl_3

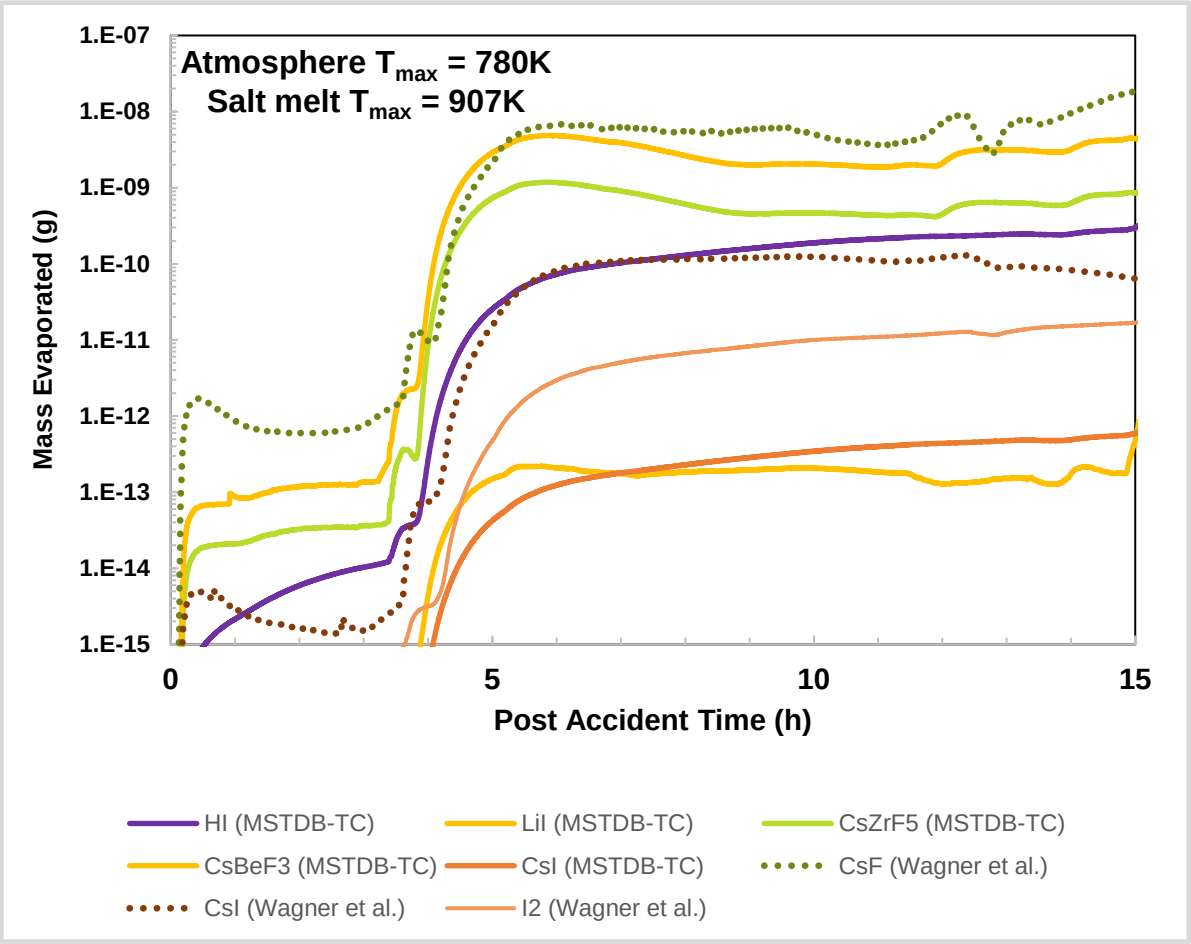


Hastelloy N* in FLiBe – 5 mol% UCl_3



Example of the Application of MSTDB-TC in MELCOR

- MELCOR has been coupled (at least manually) with MSTDB-TC and used to compute fission product release rates
- In an earlier effort by Wagner et al.* MELCOR was exercised using MSRE conditions and Antoine-type vapor pressure relations
- That effort limited database could not consider complex species
- Low release rates were found from both the approach of Wagner et al. and in use of the more extensive MSTDB-TC database



***MELCOR Accident Progression and Source Term Demonstration Calculations for a Molten Salt Reactor, Kenneth Wagner, Brad Beeny, Troy Haskin David Luxat, Rod Schmidt, SAND2023-01803 (April 2023)**

FY24 Efforts

L3 Milestone: *Complete the assessment of CeF_3-UF_4: LaF_3-UF_4; $BaCl_2$-UCl_3; $SrCl_2$-UCl_3; $LaCl_3$-UCl_3; $CeCl_3$-UCl_3; $ZrCl_4$-(NaCl, KCl, $MgCl_2$, UCl_3); NaCl-$LaCl_3$; $MgCl_2$-$LaCl_3$ systems and their inclusion in MSTDB-TC. 9/30/2024*

Workshop on Measurement and Analysis of Thermochemical & Thermophysical Properties of Molten Salts

The meeting will be solely virtual

10 AM – 3 PM Eastern US Time, July 16-17, 2024

New capabilities acquired in FY24:

- Setaram Calvet DSC capable to 825°C for accurate Cp measurements
- Elementrac fusion analysis instrument to measure oxygen and hydrogen content in salts
- High temperature XRD using sealed fused silica capillaries

Data Needs USC Cannot Satisfy

- Priority information required for MSTDB-TC beyond USC scope/capability to determine
  - Improved phase equilibria, enthalpies of mixing, Cp for the intermediate compounds for $PuCl_3$ systems with LiCl, NaCl, KCl, $MgCl_3$
  - Relevant phase equilibria and thermal values
    - UI_3-$UF_{3,4}$; UI_3-$UCl_{3,4}$; BeI_2-BeF_2
  - Experimental phase equilibria for Be-containing systems
    - Resolving BeF_2 melting temperature
    - BeF_2-CrF_2; BeF_2-FeF_2; and BeF_2-NiF_2
    - LiF-BeF_2-CrF_2; LiF-BeF_2-FeF_2; and LiF-BeF_2-NiF_2

USC General Atomics Center

<u>MSR Project Participants</u>
Juliano Schorne-Pinto
Co-developer of MSTDB-TC
Mina Azizha
Ronnie Booth
Clara Dixon
Zachary Gardiner
Amir Mofrad
Aiswarya Padinhare Manissery
Jorge Paz Soldan Palma
Jack Wilson

Questions

Your email Address

U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY