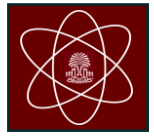


General Atomics SmartState Center for Transformational Nuclear Technologies

The Thermochemical Molten Salt Database: *MSTDB-TC*

Ted Besmann
University of South Carolina

NEUP Nuclear Energy University Program
U.S. Department of Energy

NEAMS
NUCLEAR ENERGY ADVANCED MODELING & SIMULATION PROGRAM

UNIVERSITY OF South Carolina

U.S. DEPARTMENT OF ENERGY
Office of NUCLEAR ENERGY

Contributors and Collaborators

T. M. Besmann, J. C. Ard, J. Schorne-Pinto, J. A. Yingling, J. C. Ard, M. Aziziha, M. S. Christian, A. Mofrad, M. A. A. Aslani, C. M. Dixon

University of South Carolina

J. W. McMurray and K. S Johnson

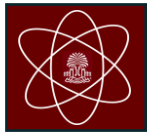
Kairos Power, LLC

Markus Piro

Ontario Tech

R. Lefebvre, C. Agca, J. McFarlane

Oak Ridge National Laboratory



General Atomics SmartState Center for Transformational Nuclear Technologies

South Carolina

Contents

- Complexity of MSR simulation
- Base salt systems
- Need for thermodynamic information/database
- Nature of a thermodynamic database
- Methodologies
- Examples of original data determinations
- Description of the database *MSTDB-TC*
- Application examples

Aircraft Nuclear Propulsion (ANP) Concept

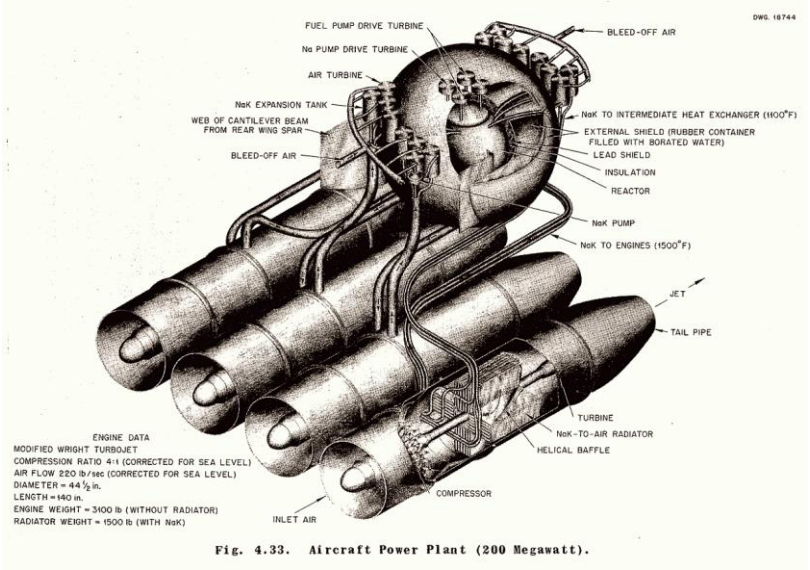
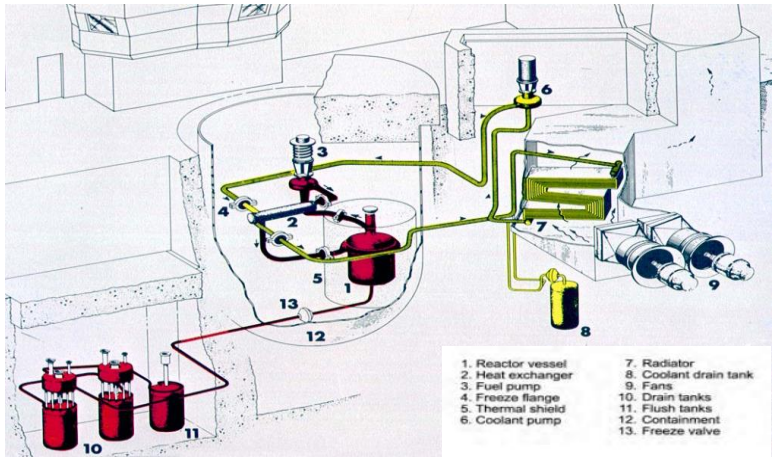


Fig. 4.33. Aircraft Power Plant (200 Megawatt).

Molten Salt Reactor Experiment (MSRE) 1965-9



General Atomics SmartState Center for Transformational Nuclear Technologies

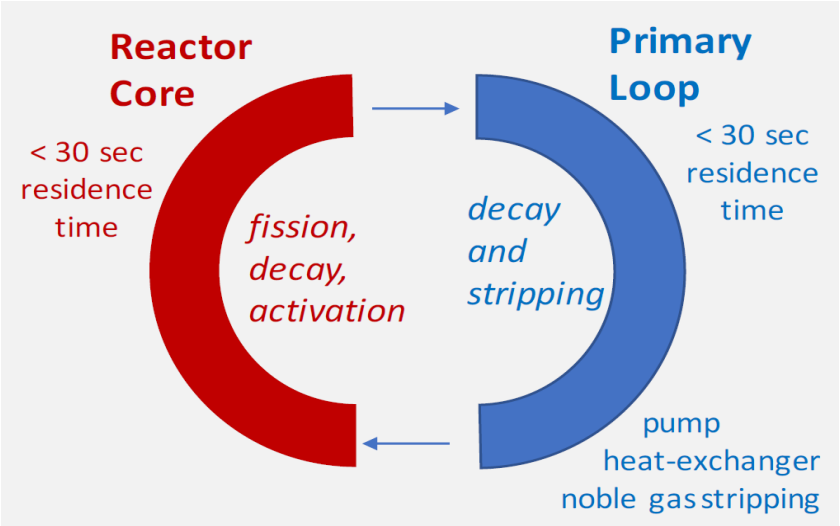
University of South Carolina

Knowing the State of the Salt (Melt Temperatures, Vapor Pressures, Reactivity) Is Obviously Necessary

Fission and Corrosion Products, Transuranics, and Contaminants (and Radiation) Govern the State of the Salt

Fission Products of Interest

- Radiological hazard Cs, I, Sr
- Reactive Zr, Te, and lanthanides
- Noble metals Rh, Ru, Tc, Pd
  - Tc, Mo can be halide as well
- Noble gases Xe, Kr, He



Corrosion Products

- Halides of Cr, Fe, Ni
- Exfoliated graphite

Contaminants

- Oxygen
- Water

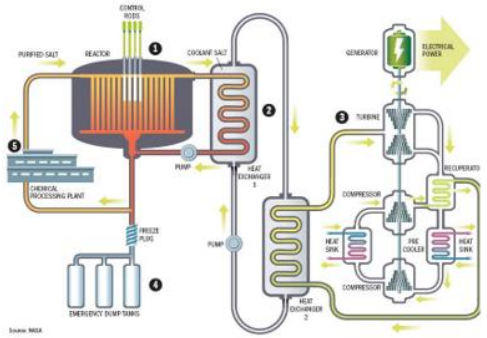
Base Salt Systems From Current Program Roadmap

Thermal spectrum: Fluoride systems

- $LiF\text{-}BeF_2\text{-}UF_3\text{-}UF_4\text{-}ZrF_4$
- $NaF\text{-}BeF_2\text{-}UF_3\text{-}UF_4\text{-}ThF_4$
- $LiF\text{-}NaF\text{-}ThF_4$
- $NaF\text{-}BeF_2\text{-}UF_3\text{-}UF_4\text{-}ThF_4$

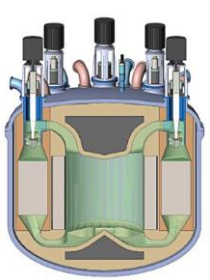
Solely heat transfer medium

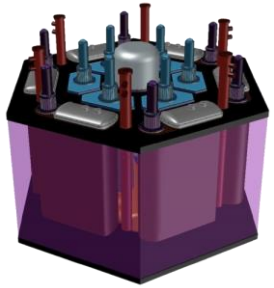
- $NaF\text{-}BeF_2$
- $LiF\text{-}BeF_2$
- $LiCl\text{-}NaCl\text{-}MgCl_2$

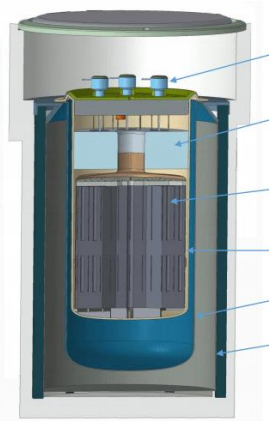


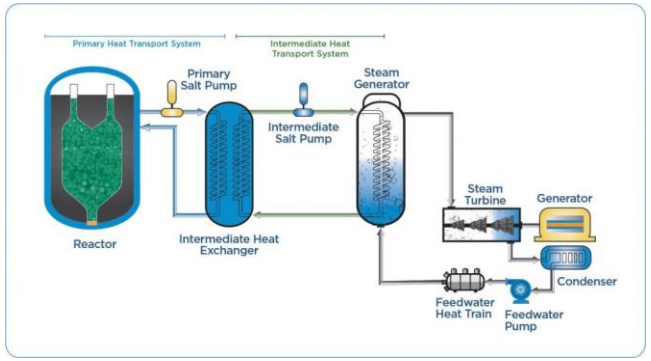
Fast spectrum: Chloride systems

- $NaCl\text{-}MgCl_2\text{-}UCl_3\text{-}UCl_4\text{-}PuCl_3$,
- $NaCl\text{-}\ ZrCl_4\text{-}UCl_3\text{-}UCl_4\text{-}PuCl_3$,
- $NaCl\text{-}AlCl_3\text{-}\ UCl_3\text{-}UCl_4\text{-}PuCl_3$,
- $NaCl\text{-}KCl\text{-}MgCl_2\text{-}UCl_3\text{-}UCl_4\text{-}PuCl_3$,
- $NaCl\text{-}KCl\text{-}ZrCl_4\text{-}UCl_3\text{-}UCl_4\text{-}PuCl_3$,
- $NaCl\text{-}KCl\text{-}AlCl_3\text{-}UCl_3\text{-}UCl_4\text{-}PuCl_3$,
- $NaCl\text{-}ThCl_4\text{-}PuCl_3$









General Atomics SmartState Center for Transformational Nuclear Technologies

University of South Carolina

Gibbs Energy Relations Allow Calculation of Equilibrium State of the Salt (Chemical/Phase Behavior)

- Salt should be near equilibrium due to high temperatures and liquid state
- Governed by their thermodynamic properties, i.e., Gibbs energies
- Computed equilibria can therefore provide
  - Local composition/speciation
  - Precipitating solid phases (melting points)
  - Phase formation
  - Chemical potentials/redox for controlling corrosion and transport;
  - Vapor pressures
  - Input for phase field calculations: Modeling nucleation and grain growth
  - Source terms for accident analysis

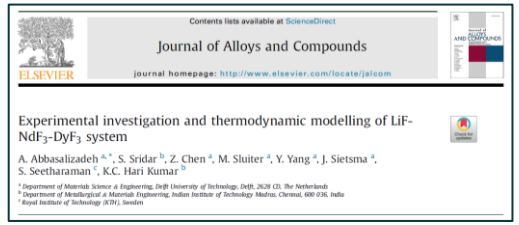
Thermodynamic Modeling Requires an Accurate, Consistent and Extensive Gibbs Energy Database

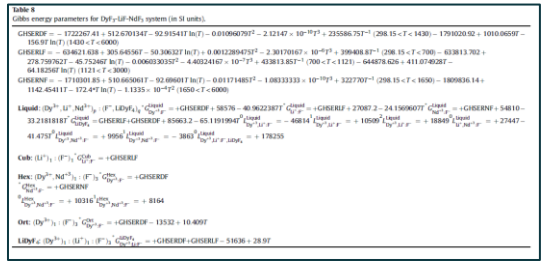
- Database consists of Gibbs energy relations for each phase and gas species
- Gibbs energy relations for (stoichiometric) compounds are obtained from
  - Directly from accurate reported values
  - Assessment of reported data and/or measurements
- Solid and liquid solutions need to be represented by models that provide Gibbs energy relations at specific temperature, pressure, and composition (gas typically an ideal solution)
  - Directly from accurate reported values consistent with basic database phase values, or
  - Reassessment of reported models using new data and consistent base values, or
  - Full assessment from reported values/new measurements using consistent base values
- Resource is the *Molten Salt Thermal Properties Database – Thermochemical* (*MSTDB-TC)*

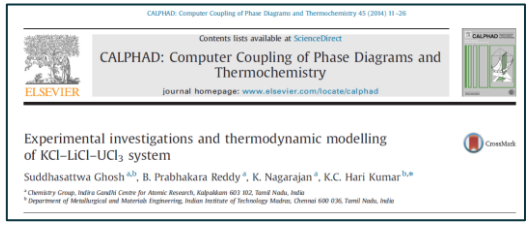
Sources of *MSTDB-TC* Values Vary From Directly Extracted From Publications to Derived From Original Measurements

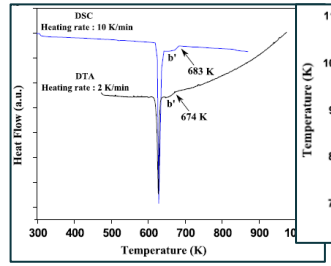
All values traceable to original sources: Information linked within the user database

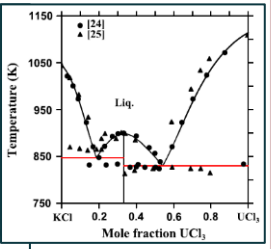
- Pure substance, single cation phase values from tabulated sources, e.g., NIST, SGTE via FactSage™
- Melt, solid solution, or complex compound models and values/parameters are
  - Obtained as is from published papers/reports
  - Determined in assessments/reassessments using values from published papers/reports
  - Computed for compounds obtained using *ab initio* modeling & used in assessments
  - Obtained using measurements for assessments from original experimental efforts





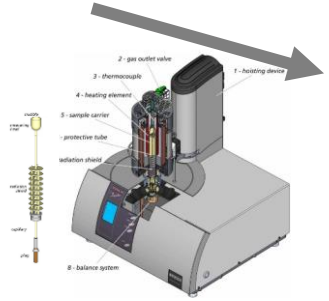


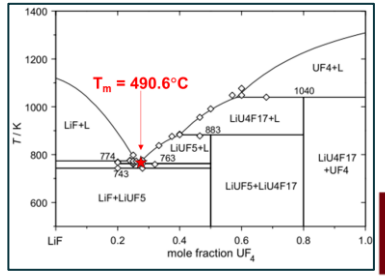


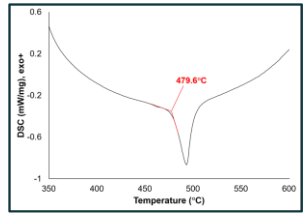


DFT

	H°0K (eV)	H°0K (J/mol)
K_2UF_6	-3.643	-3163464.3
K_3UF_7	-3.523	-3739095.7
$K_7U_6F_{31}$	-	
KU_2F_9	-3.858	-4466884.5







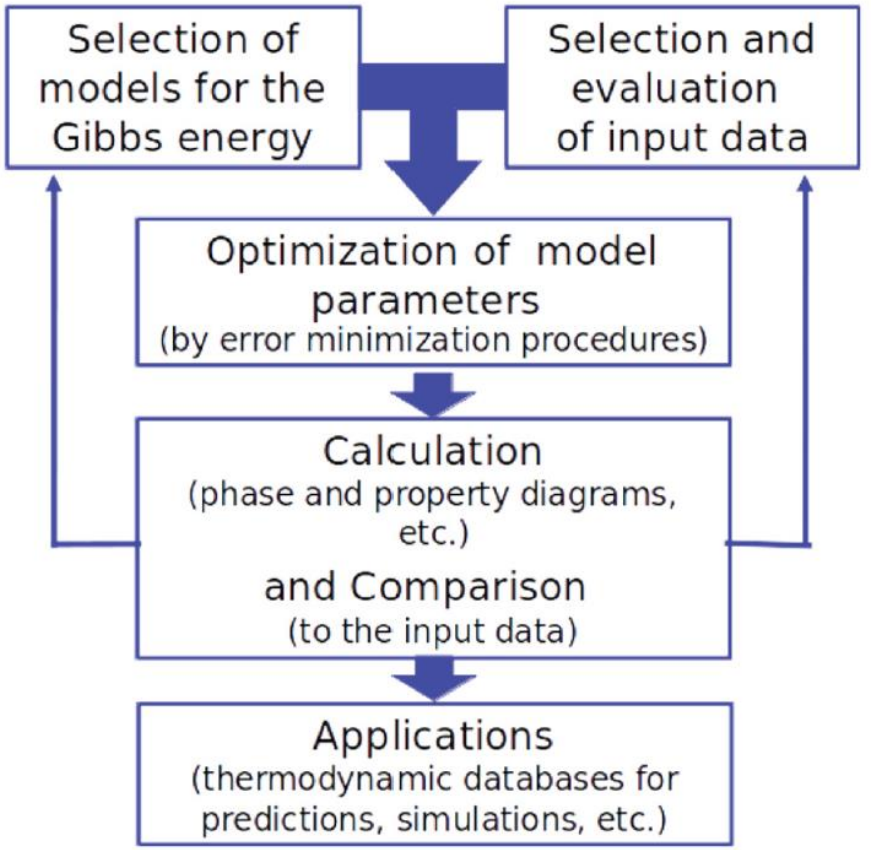
General Atomics SmartState Center for Transformational Nuclear Technologies

University of South Carolina

Original Gibbs Energy Relations Obtained from Thermochemical Assessments

- Assessment (CALPHAD) Methodology
  - Selected models contain adjustable parameters
  - Optimized to experimental data and/or first principles calculational results
  - Quality based on reproducing experimental observations
- Sublattice models used for crystalline phases and non-salt liquids
  - Compound energy formalism: $(A,B)_k(C,D)_l(E,F)_m$
  - Two-sublattice partially ionic liquid model: $\left(C_i^{\nu_i+}\right)_P \left(A_j^{\nu_j-}, Va, B_k^0\right)_Q$
- Molten salts challenging as they exhibit short range ordering (SRO) and thus require use of a model that captures SRO

CALPHAD Method



Salt Melt Quasichemical Model Accounts for SRO, and Can Accommodate Variable Atom Coordination

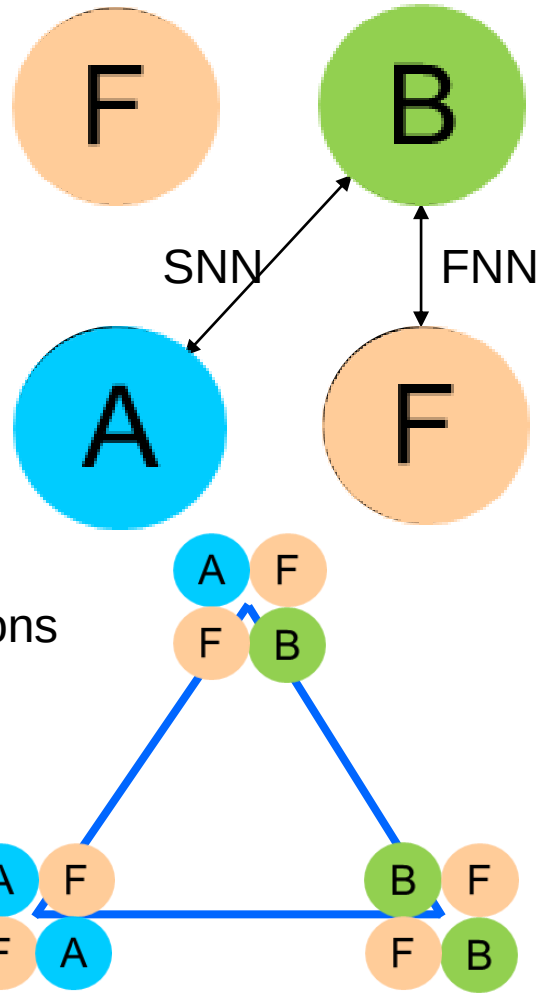
- First sublattice contains all cations (Li, Na, U, Th, etc.); second contains common anion (e.g., F or Cl)

$$G = (n_A G_A^{\circ} + n_B G_B^{\circ}) - T\Delta S^{config} + (n_{AB}/2)\Delta G_{AB}$$

- Excess Gibbs energy subsystem end-member interaction parameters each optimized from experimental/1st principles computes/estimated data
- Quadruplets: A_2F_2; B_2F_2; ABF_2
  - FNN interactions between cations and anions
  - SNN interactions between cations
- Cation-cation coordination numbers defined for each binary sub-system:

$$Z^A_{AB/FF},\ Z^B_{AB/FF}$$

where charge neutrality requires: $\frac{q_A}{Z^A_{AB/FF}} + \frac{q_B}{Z^B_{AB/FF}} = \frac{q_F}{Z^F_{AB/FF}} + \frac{q_F}{Z^F_{AB/FF}}$



General Atomics SmartState Center for Transformational Nuclear Technologies

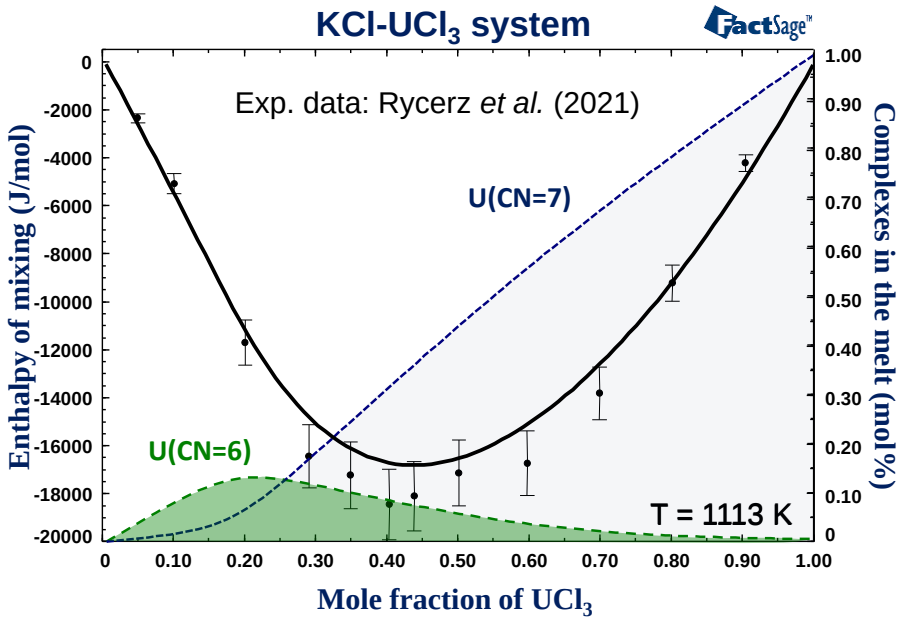
E. Capelli, O. Benes, R.J.M. Konings, Journal of Nuclear Materials 449 (2014) 111-121.

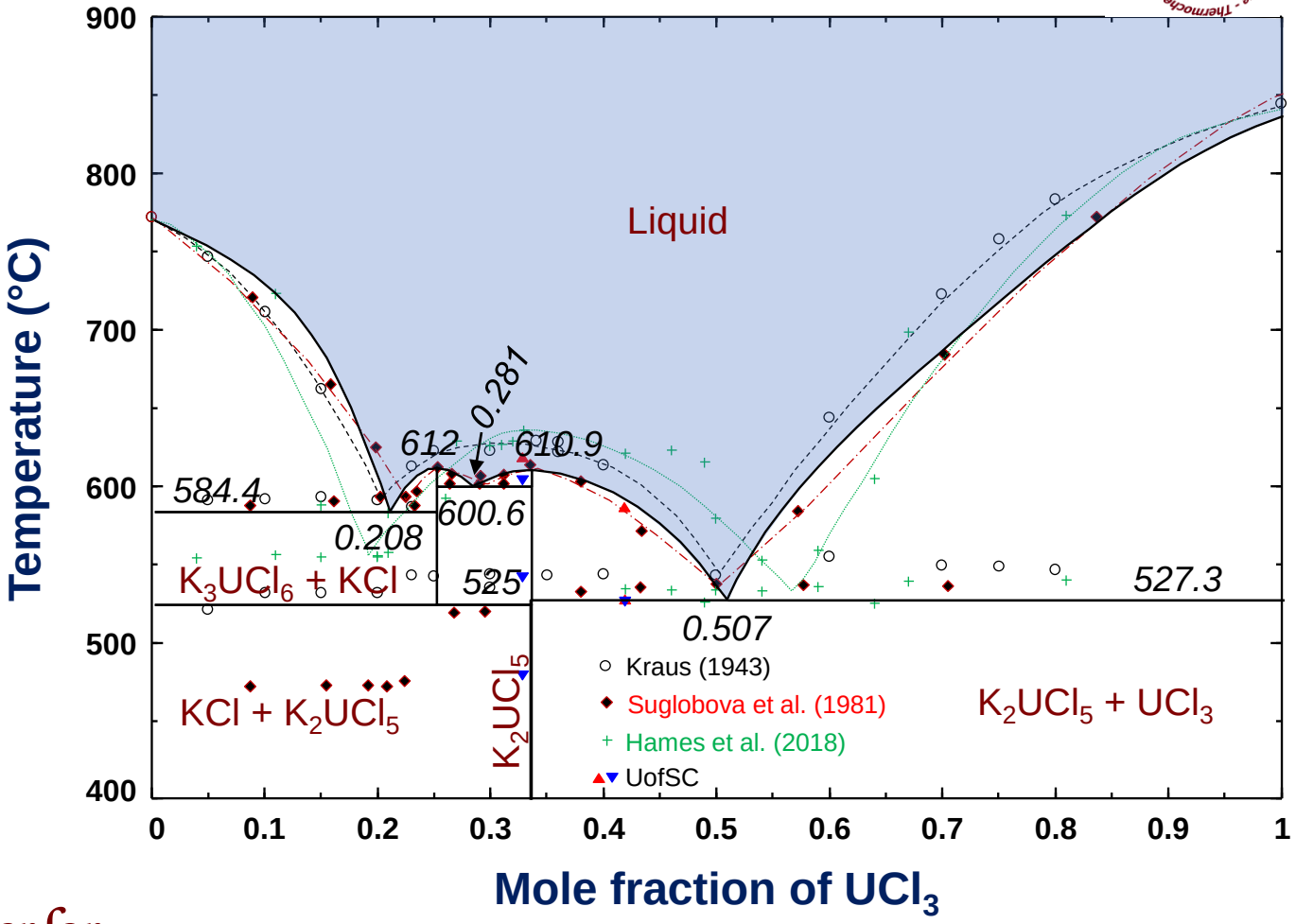
South Carolina

Model Generation (Assessments) Use Thermodynamic/Structural/Phase Information to Obtain Relations: Example KCl-UCl_3

Reported Thermodynamic/Structural Measurements:

- Rycerz *et al.* (2021)
  - Heat of mixing ($\Delta_{mix}H$) for KCl-UCl_3 melt
  - Estimate for Gibbs energy for **K_3UCl_6**
- Exptl. Δ_fH_{298} for **K_2UCl_5**
- UCl_3 coordination numbers 6 and 7





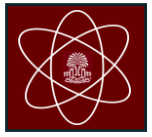
General Atomics SmartState Center for Transformational Nuclear Technologies

University of South Carolina

MSTDB-TC not Export Controlled and Should be Available Cost-Free on the Code.ornl Github

- *MSTDB-TC* Follows the FactSage ASC II Format (.dat)
- Database provides
  - Thermodynamic functions readable by FactSage™ and open-source code Thermochimica
  - Pseudo-binary and higher order system data
    - Reference values from literature with sources
    - Original measurements including uncertainties
    - Details of function fitting and uncertainties
- All systems validated via reproduction of accepted phase equilibria
  - Verified via examination of all systems by third-party (ORNL)

```
System U-F-Li
    3    2    2    3   12
 U                        F                        Li
   238.02891000             18.99840320              6.94100000
   6   1   2   3   4   5   6
   6   1   2   3   4   5   6
 gas_ideal
 IDMX
 LiF
   1  1    0.0    1.0    1.0
  6000.0000     -351581.57      37.443358     -35.397917     -.93533200E-03
 0.27571767E-07 0.00000000
UF4
   1  1    1.0    4.0    0.0
  6000.0000     -1639992.8      343.21185     -103.82600     -.47745000E-02
 0.24183333E-06  510660.00
LIQUsoln
 SUBG
  2.40000
   2   3
 Li//F
   1  1    0.0    1.0    1.0
  2500.0000     -617790.20      386.90980     -64.182999     0.00000000
 0.00000000     0.00000000
  1.00000      1.00000     0.000000     0.000000     0.000000
 U//F
   1  1    1.0    4.0    0.0
  2500.0000     -1966756.7      1054.9383     -174.74000     0.00000000
 0.00000000     0.00000000
  1.00000      4.00000     0.000000     0.000000     0.000000
   2   1
 Li                       U
 F
  1.00000      4.00000
   1   2
  1.00000
   1
   1   2
   1   1
   1   1   3   3  6.0000000      6.0000000      6.0000000      6.0000000
   2   2   3   3  6.0000000      6.0000000      1.5000000      1.5000000
   1   2   3   3  2.0000000      6.0000000      1.7142857      1.7142857
   3
 G   1   2   3   3   0   0   0   0
 0.00000000       1.00 0.00000000       1.00 0.00000000       1.00
 0.00000000       0.00 0.00000000       0.00 0.00000000       0.00
   0   0 -16108.400     0.00000000     0.00000000     0.00000000
```



General Atomics SmartState Center for Transformational Nuclear Technologies

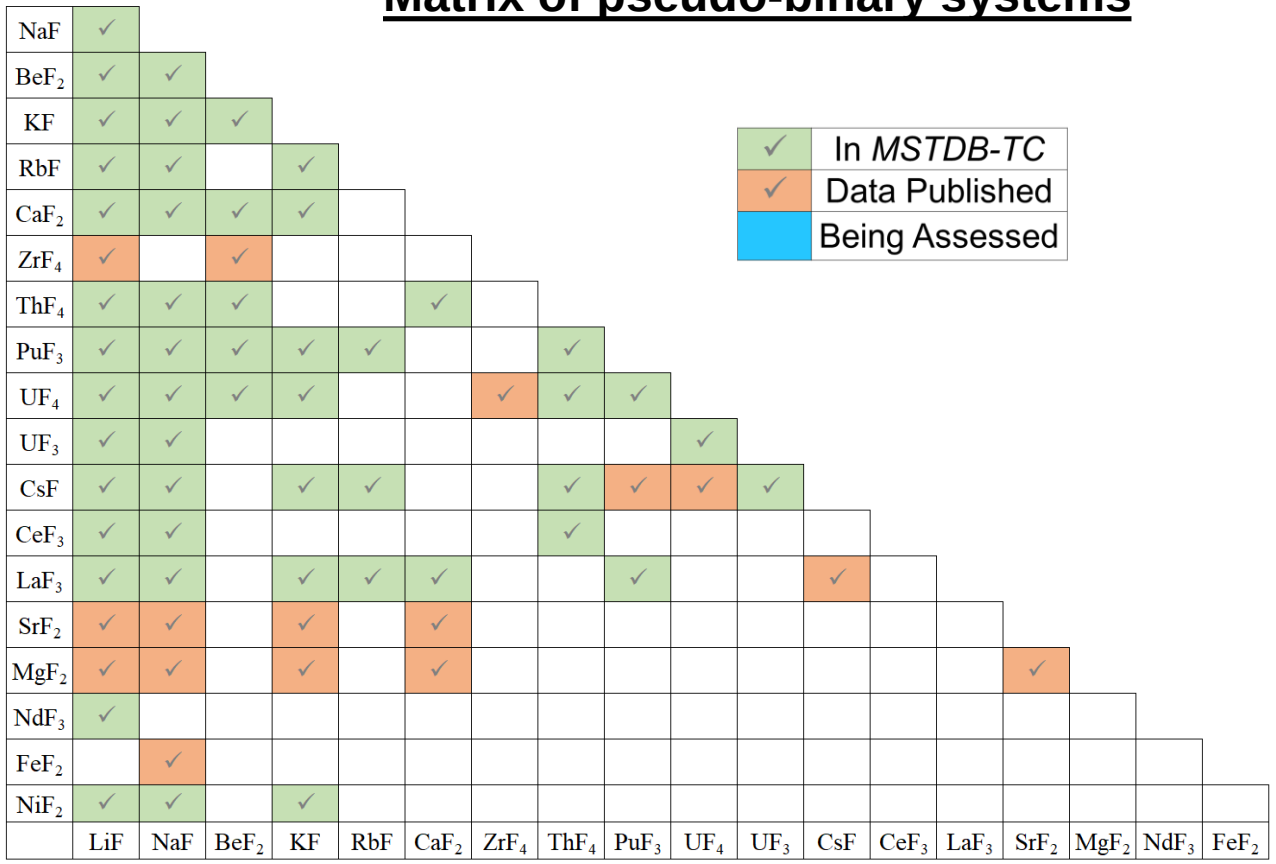
South Carolina

Fluoride Systems Content of *MSTDB-TC* (Ver 1.2): Be-Ca-Ce-Cs-K-La-Li-Mg-Na-Ni-Nd-Pu-Rb-Th-U-F

Pseudo-ternary and higher order systems

- BeF2-LiF-NaF
- BeF2-LiF-PuF3
- BeF2-LiF-ThF4
- BeF2-LiF-UF4
- BeF2-NaF-PuF3
- BeF2-NaF-UF4
- BeF2-ThF4-UF4
- CaF2-KF-NaF
- CaF2-LaF3-LiF
- CaF2-LaF3-NaF
- CaF2-LiF-KF
- CaF2-LiF-ThF4
- CeF3-LiF-ThF4
- CsF-LiF-KF
- LaF3-LiF-NaF
- LiF-KF-NaF
- LiF-KF-RbF
- LiF-NaF-CeF3
- LiF-NaF-PuF3
- LiF-NaF-RbF
- LiF-NaF-ThF4
- LiF-NaF-UF4
- LiF-PuF3-ThF4
- LiF-PuF3-UF4
- LiF-ThF4-CaF2
- LiF-NaF-BeF2-ThF4-PuF3-UF4
- LiF-NaF-BeF2-KF-PuF3-UF4
- LiF-NaF-KF-CsF-ThF4-PuF3

Matrix of pseudo-binary systems



General Atomics SmartState Center for Transformational Nuclear Technologies

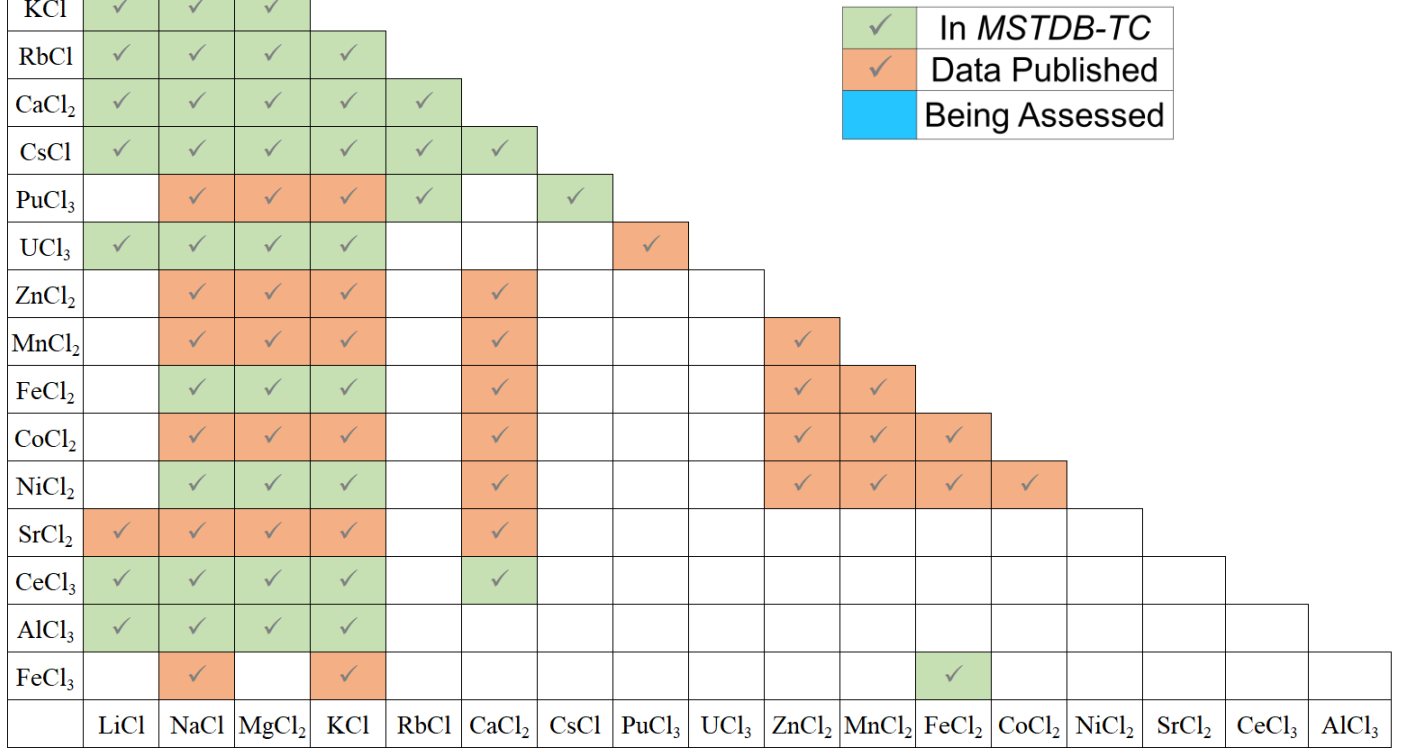
University of South Carolina

Chloride Systems Content of *MSTDB-TC* (Ver 1.2) : Cs-K-Li-Mg-Na-Pu-U-Cl

Pseudo-ternary and higher order systems

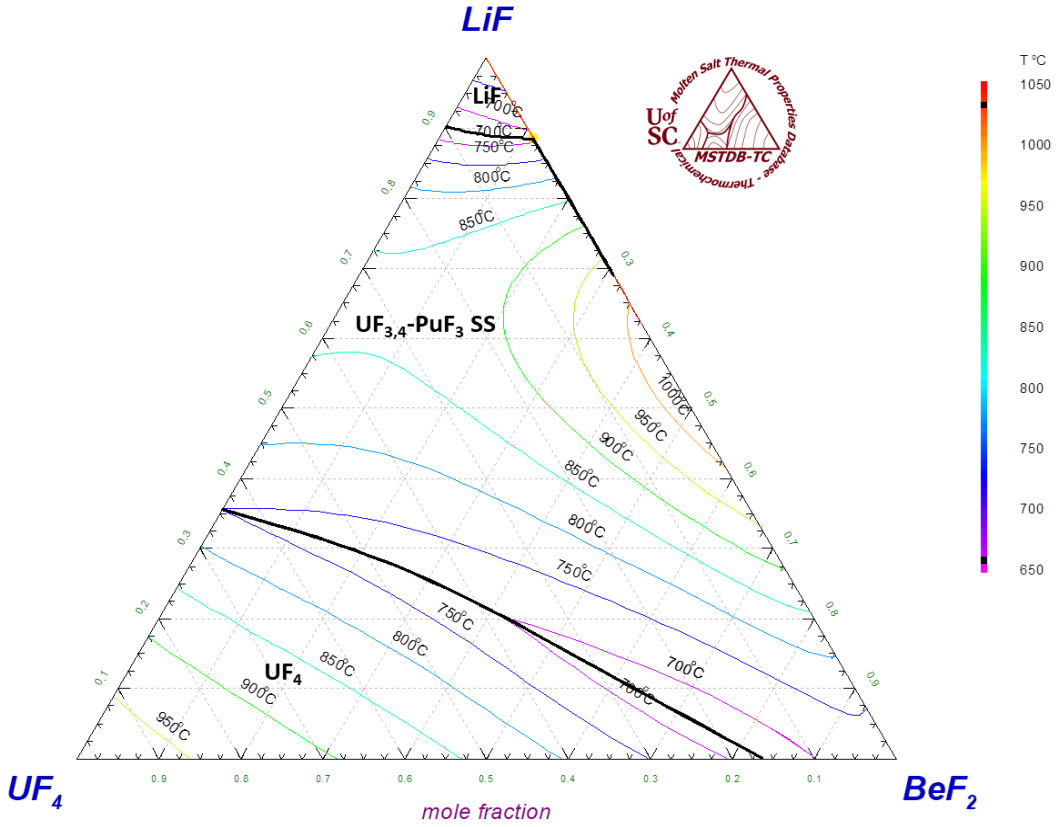
- CeCl3-KCl-LiCl
- CeCl3-KCl-MgCl2
- CeCl3-KCl-NaCl
- CeCl3-LiCl-MgCl2
- CrCl2-KCl-MgCl2
- KCl-LiCl-UCl3
- LiCl-NaCl-MgCl2-KCl-PuCl3-UCl3
- LiCl-NaCl-MgCl2-KCl-CeCl3

Matrix of pseudo-binary systems

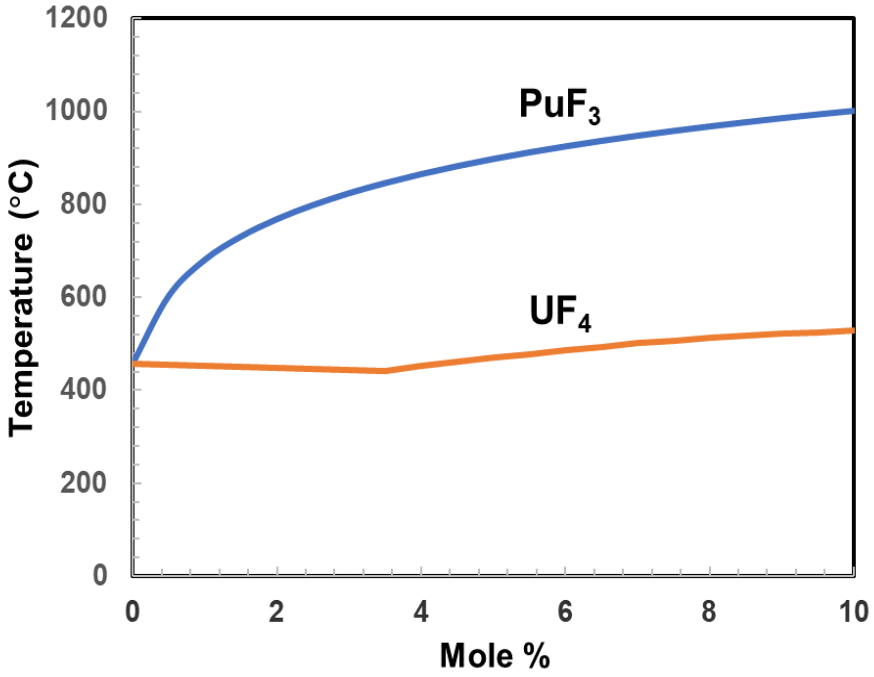


Thermochemical Calculations Using *MSTDB-TC* Provide Insight Relative to General Salt Behavior - Examples

LiF-BeF_2-UF_4 liquidus projections for fixed content of 10 mol% UF_3 + 1 mol% PuF_3



Influence on FLiBe liquidus temperature from added UF_4 or PuF_3

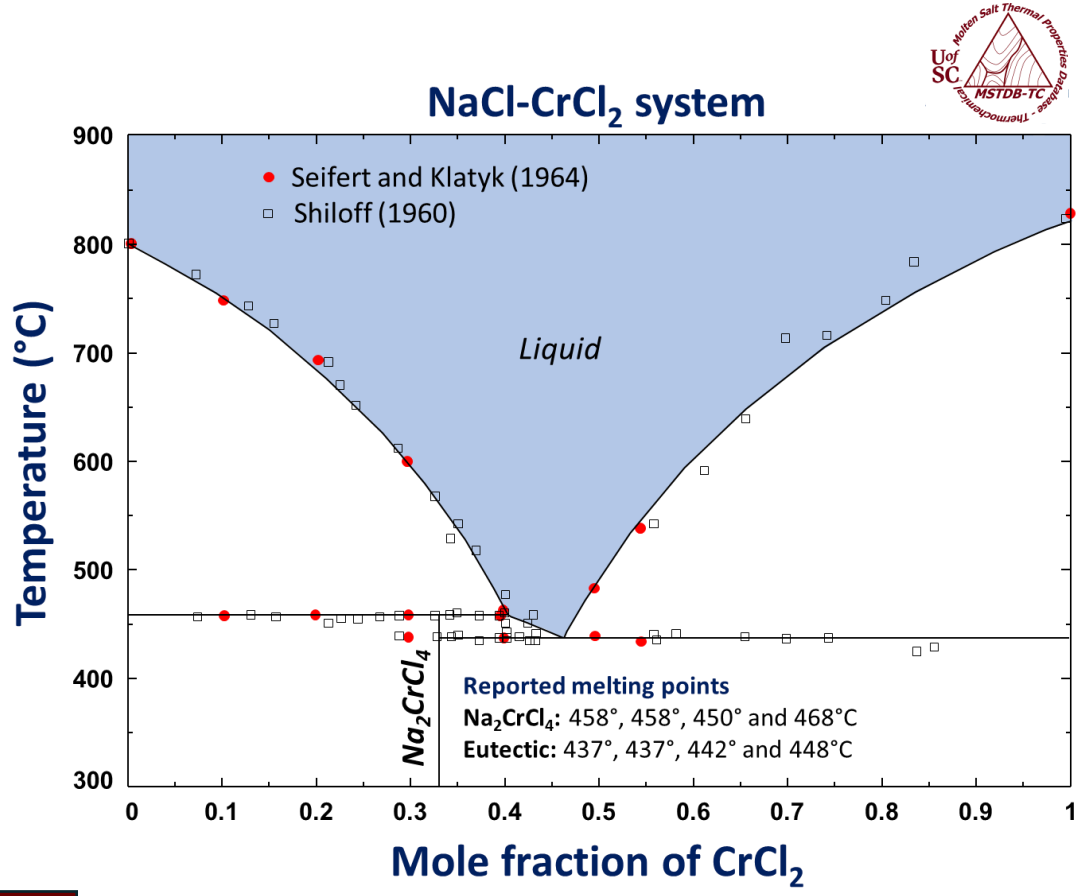


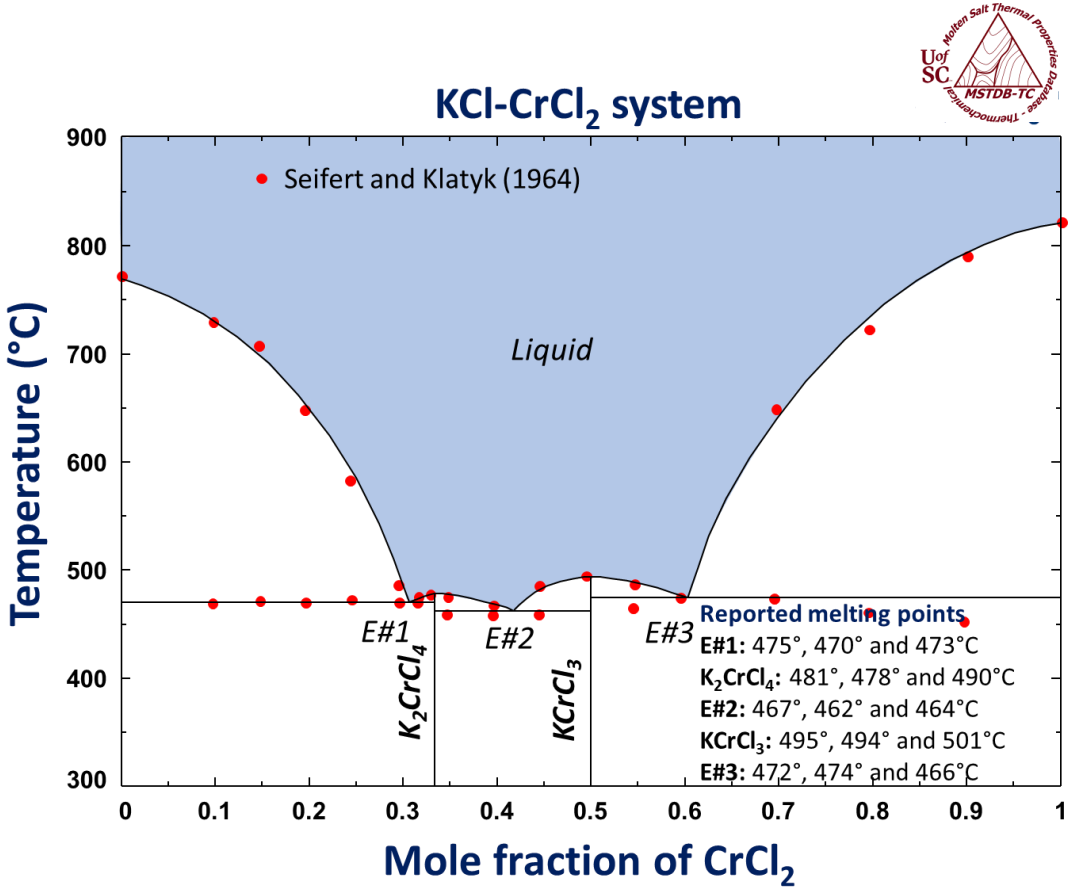
General Atomics SmartState Center for Transformational Nuclear Technologies

University of South Carolina

Current Efforts (NEUP) Adding Gibbs Functions/Models for Base Salt Systems with Corrosion-Relevant Components

Diagrams computed from original *MSTDB-TC* functions for 2 important pseudo-binary systems





General Atomics SmartState Center for Transformational Nuclear Technologies

University of South Carolina

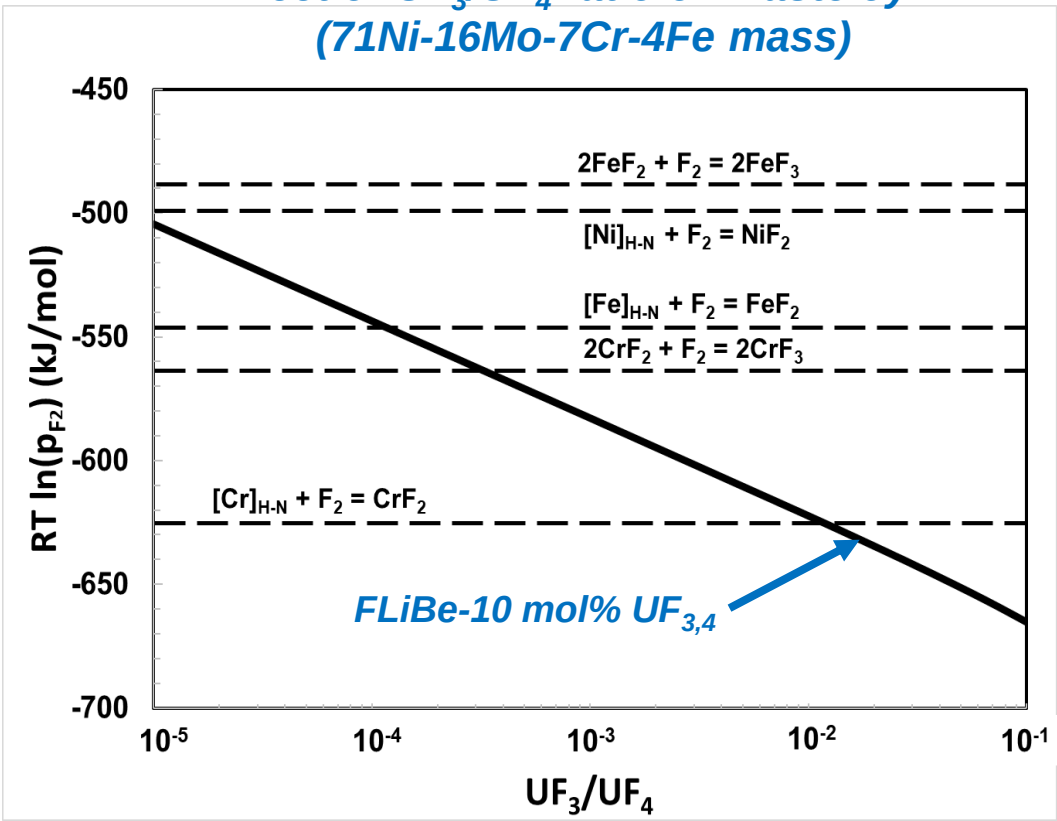
Example of Use of Salt and Alloy Gibbs Energy Functions/Models to Provide Corrosion Potential

- Fluorine potential can be calculated for FLiBe equilibrated with Hasteloy-N
  - Salt Gibbs energy functions/models from MSTDB-TC for LiF-BeF_2-$UF_{3,4}$
  - Preliminary models adopted for Cr, Fe, Ni, and Mo fluorides with LiF-BeF_2
  - Sublattice models and compound values for multiple alloy and intermetallic phases of Fe-Ni-Cr-Mo from SGTE* database for Hasteloy-N

- Results are
  - LiF-BeF_2-$UF_{3,4}$ fluorine potential vs UF_3/UF_4
  - Minimum fluorine potentials at which the alloy constituents form fluoride species in the melt

***Scientific Group Thermodata Europe**

Computed RT ln(p_{F2}) at 750 ℃ for FLiBe-10 mol% $UF_{3,4}$: Effect of UF_3/UF_4 ratio on Hasteloy-N (71Ni-16Mo-7Cr-4Fe mass)



General Atomics SmartState Center for Transformational Nuclear Technologies

University of South Carolina

Molten Salt Thermal Properties Working Group

Workshop on Molten Salt Thermal Properties – 2021

VIRTUAL MEETING

1-5 PM EST Nov. 15-17

- Experimental methods, instruments and techniques
- Salt system measurements and data reduction
- First principles and CALPHAD modeling
- Property databases
- Round-robin exercise
- Opportunities for collaboration

Invited speakers

- Patricia Paviet, PNNL, NTD DOE Molten Salt Reactor Campaign
- David Luxat, SNL, Manager, Severe Accident Modeling/Analysis
- Chris Stanek, LANL, NTD DOE NEAMS Program
- Jim Wishart, BNL, Dir. DOE-BES Center for Molten Salts in Extreme Environments

NO COST – BUT REGISTRATION REQUIRED

https://www.surveymonkey.com/r/CYZ336Y

Contact Ted Besmann: besmann@sc.edu

General Atomics SmartState Center for Transformational Nuclear Technologies

U of SC South Carolina

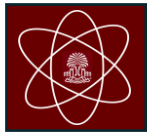
Summary and Conclusions

- Thermochemical behavior of base salts together with fission products, corrosion products, and contaminants is important for MSR modeling and simulation
- Assessments allow generation of Gibbs energy relations for phases to compute overall system equilibria and offer values required for modeling such as phase field
- *MSTDB-TC* is designed to be source of thermodynamic data to support those efforts
- Gibbs energy functions/models for base salts being expanded in continuing program with emphasis on corrosion- and safety-related systems

NEUP Nuclear Energy University Program
U.S. Department of Energy

Research Supported by the U.S. DOE Office of Nuclear Energy, Nuclear Energy Advanced Modeling and Simulation Program and the Nuclear Energy Universities Program, project DE-NE0008985

NEAMS
NUCLEAR ENERGY ADVANCED MODELING & SIMULATION PROGRAM



General Atomics SmartState Center for Transformational Nuclear Technologies

U of SC South Carolina

General Atomics Center Researchers and Students

➢ *We are looking for new post-docs to join us!* ➢

General Atomics SmartState Center for Transformational Nuclear Technologies

U of SC South Carolina