Development and Application of a Molten Salt Chemistry Database in Modeling MSR Performance

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Molten Salt Reactor Workshop 2018

Creating a Self-Sustaining Environment for MSR Success

October 3-4, 2018

What is Important? – Thermophysical and Thermochemical Properties

Free energy models
- Melting Point
- Boiling Point
- Density
- Heat capacity
- Corrosion reactions/redox

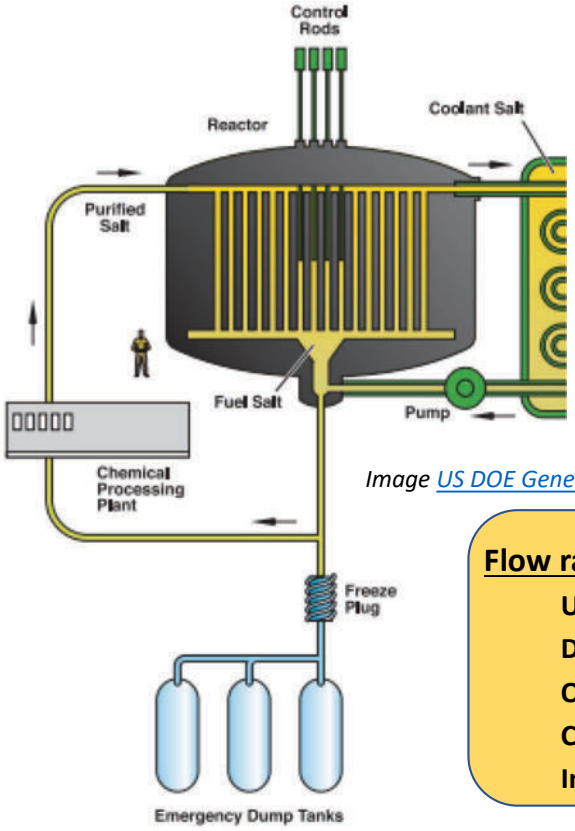


Image US DOE Generation IV Roadmap

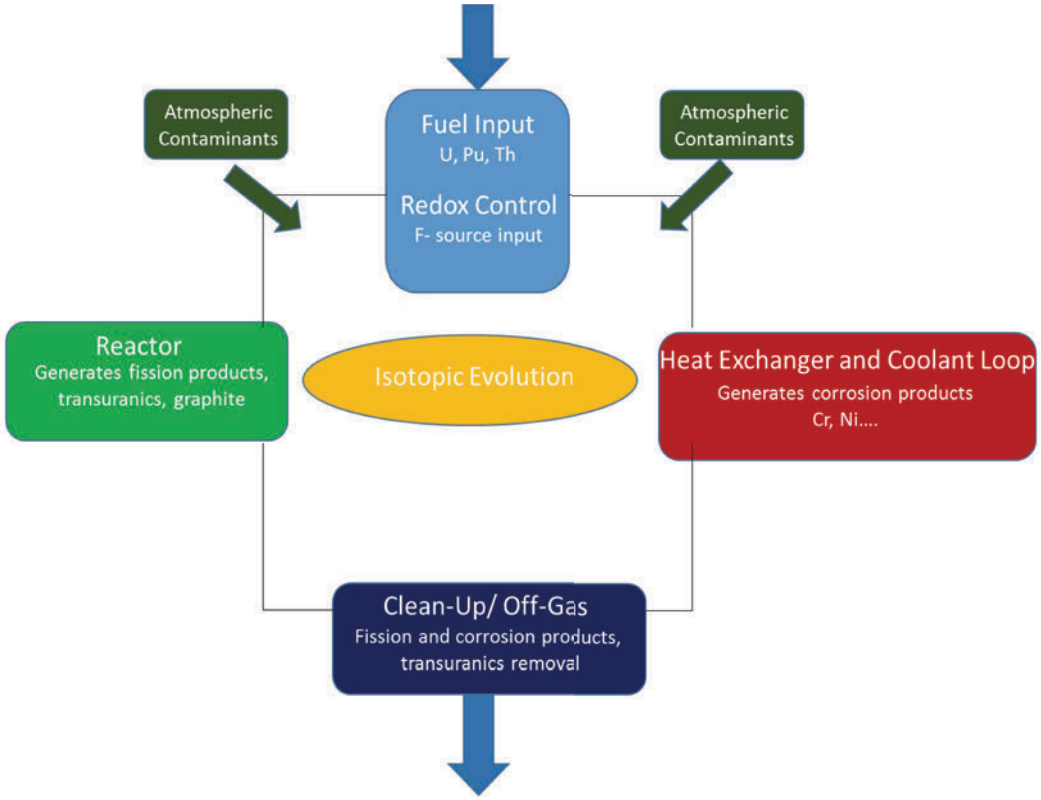
Source Terms: Changes in chemistry/speciation under differing accident scenarios
- Oxidation/partial oxidation
- Vapor species/pressures
- Surface/material adsorption
- Hydration

Thermophysical values
- Viscosity
- Fluid dynamics
  - e.g., Nu, Re, Pr
- Opacity
- Thermal expansion coefficient
- Thermal conductivity

Flow rate of the salts/distances
- Unstable isotopes have complex influences
- Delayed neutrons emitted outside the reactor core
- Other neutrons may be released after emitters circulate
- Composition of the salt evolves spatially and temporally
- Influences reactor behavior and source terms

Chemistry Databases Provide Properties to Reactor Simulations

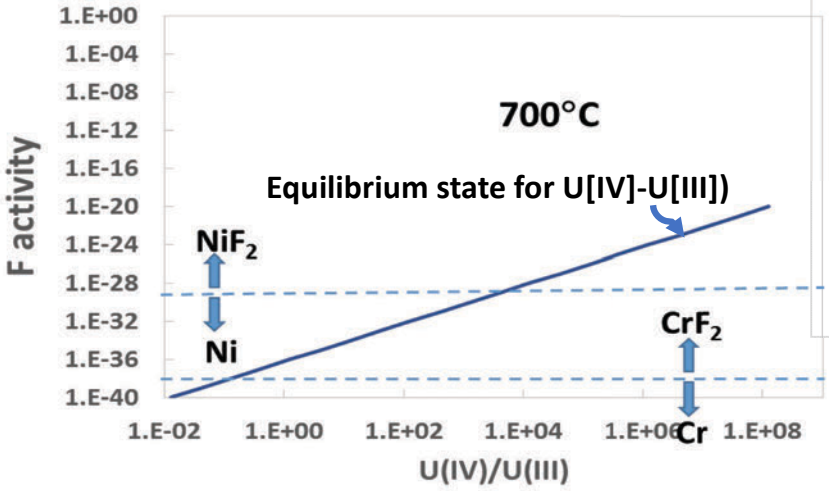
- Approach is for database to have two components
  - Thermochemical: Free energy models & values
  - Thermophysical: Phenomenological relations
- Will maintain consistent, accurate set of values and models for all elements/materials of interest
- Include temperature and compositional dependence to allow coupling with time dependent behavior
- Can be incorporated in reactor simulation codes for accurate representation of reactor/fuel performance
- Provide basis for reliable prediction of behavior outside empirical data envelope



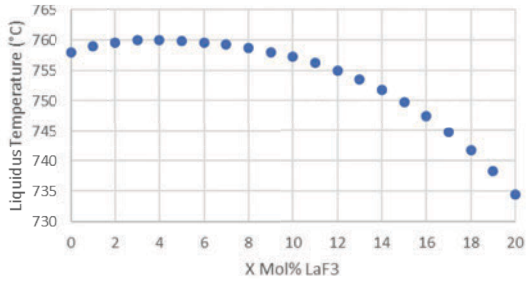
Thermochemical Database Component: MSR-Related Example

Computed liquidus projections for UF_4-LiF-ThF_4
Minor mole fractions of PuF_4 (0.1) and $CrNiMoF_3$ (0.0001)

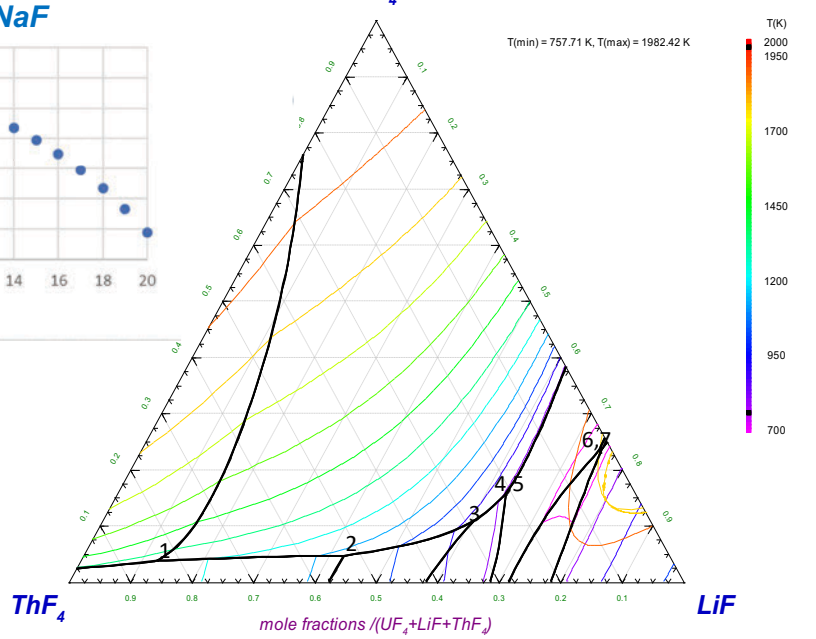
Corrosion potential:
Fluorine activity vs. redox (ratio of U[IV] to U[III])



Liquidus change with La addition to UF_4-20 mol%NaF



UF_4 - LiF - ThF_4 - $CrNiMoF_3$ - PuF_4
…uid), $CrNiMoF_3$/Z (mol/mol) = 0.0001, PuF_4/Z (mol/mol) = .
Z=(UF_4+LiF+ThF_4), 1 atm



Framework for a Molten Salt Reactor Thermochemical Database, Formalisms, and Tabulated Systems of Interest

Tasks

- Identify salt systems and compositions that constitute the fundamental constituents of a thermochemical database.
- Identify important, common non-fuel or coolant constituents (e.g., fission products, transuranics, contaminant oxygen and nitrogen, corrosion products chromium, nickel…).
- Utilizing the Chemsage thermochemical database as a framework for a stand-alone *Molten Salt Thermochemical Database* (*MSTDB*), generate an example database populated with sufficient constituents to demonstrate capability.
- Recommend a set of internally consistent thermochemical models to effectively describe the liquid salt systems, gas phase, and relevant solids expected under operating, accident, and ex-situ reactor fuel processing.

Development of *Molten Salt Thermodynamic Database* (*MSTDB*) Considers Inventory and Disposition of Constituents

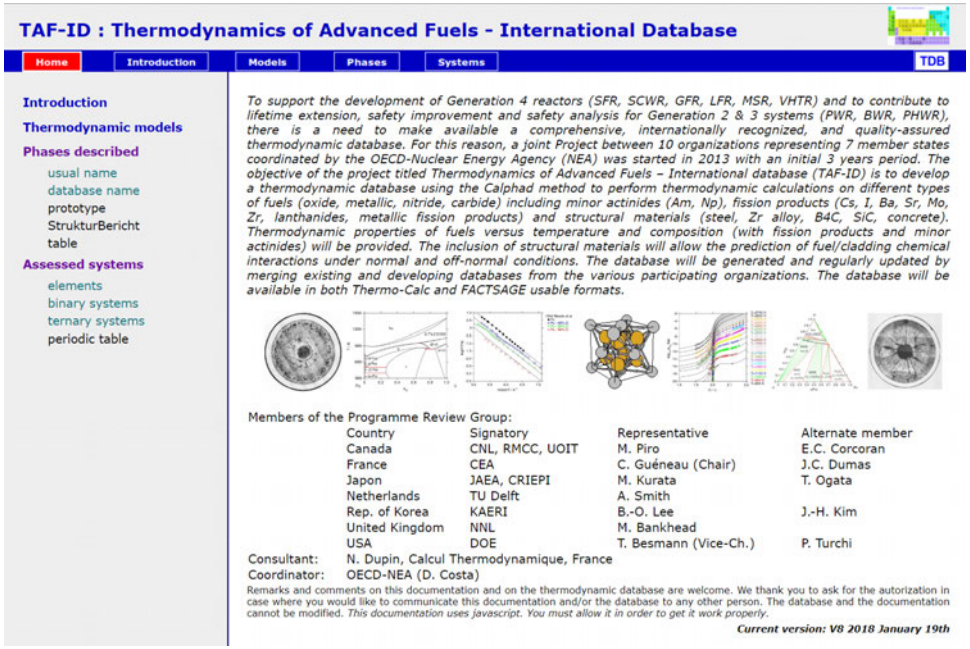
Chain	Isotope	Half-life	Fraction	^{233}U	^{235}U	^{239}Pu
89	Sr	52 days	1	5.86	4.79	1.711
90	Sr	28.1 years	1	6.43	5.77	2.21
91	Sr	9.67 hr	1	5.57	5.81	2.43
91	Y	59 days	(1.0)[c]	5.57	5.81	2.43
95	Zr	65 days	1.0	6.05	6.20	4.97
95	Nb	35 days	(1.0)	6.05	6.20	4.97
99	Mo	67 hr	1.0	4.80	6.06	6.10
103	Ru	39.5 days	1.0	1.80	3.00	5.67
106	Ru	368 days	1.0	0.24	0.38	4.57
109	Ag	Stable	(91 b + resonance)	0.044	0.030	1.40
110	Ag(m)	253 days				
111	Ag	7.5 days	1	0.0242	0.0192	0.232
125	Sb	2.7 years	1	0.084	0.021	0.115
127	Te(m)	100 days	0.22	0.60	0.13	0.39
129	Te(m)	34 days	0.36»	2.00	0.80	2.00
132	Te	3.25 days	1.0	4.40	4.24	5.10
131	I	8.05 days	1.0	2.90	2.93	3.78
133	Cs	Stable	(32 b + resonance)	5.78	6.61	6.53
134	Cs	750 days				
137	Cs	29.9 years	1	6.58	6.15	6.63
140	Ba	12.8 days	1	5.40	6.85	5.56
141	Ce	32.3 days	1	6.49	6.40	5.01
144	Ce	284 days	1	4.61	5.62	3.93
147	Nd	11.1 days	1	1.98	2.36	2.07
147	Pm	2.65 years	1	1.98	2.36	2.07

Fission Product Group	Example Isotopes	In Salt	To Metal	To Graphite	To Off-Gas
Stable salt seekers	Zr-95, Ce-144, Nd-147	~99	Negligible	<1 (fission recoils)	Negligible
Stable salt seekers (noble gas precursors)	Sr-89, Cs-137, Ba-140, Y-91	Variable/$T_{1/2}$ of gas	Negligible	Low	Variable/$T_{1/2}$ of gas
Noble gases	Kr-89, Kr-91, Xe-135, Xe-137	Low/$T_{1/2}$ of gas	Negligible	Low	High/$T_{1/2}$ of gas
Noble metals	Nb-95, Mo-99, Ru-106, Ag-111	1-20	5-30	5-30	Negligible
Tellurium, antimony	Te-129, Te-127, Sb-125	1-20	20-90	5-30	Negligible
Iodine	1-131,1-135	50-75	<1	<1	Negligible

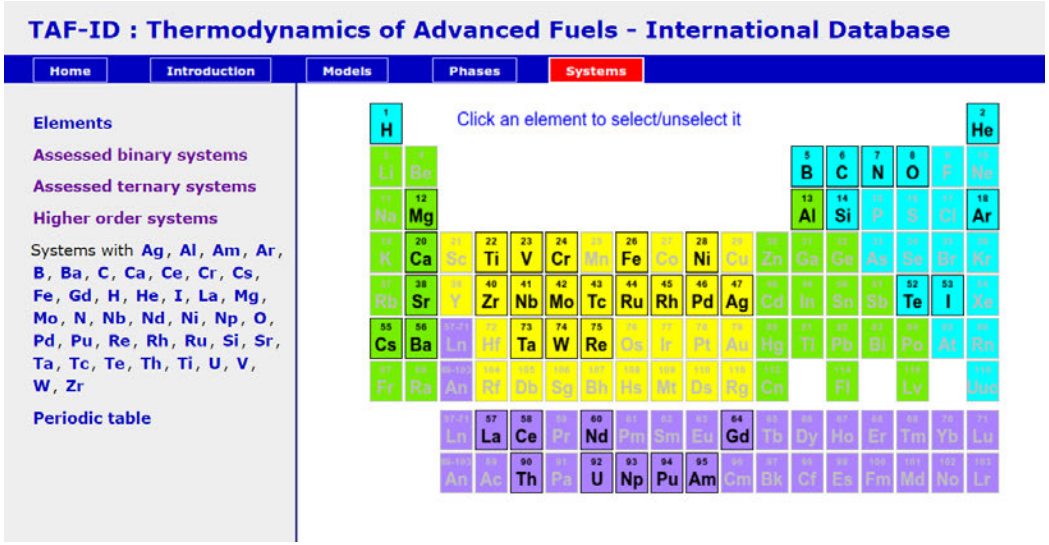
Fission Product Behavior in the Molten Salt Reactor Experiment
ORNL-4865— Molten Salt Reactor Technology

NEA Database Thermodynamics for Advanced Fuels-International Database (TAF-ID) as Model for *MSTDB*

Opening page



Selecting system data



MSTDB Adopted ChemSage Format: FactSage® and Thermochimica

```
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
```

- Accommodates envisioned phase thermochemical models
  - Gaseous
  - Liquid
  - Complex crystalline
- Uses inclusive phase models
  - Modified quasi-chemical in quadruplet assumption (molten salt)
  - Two sublattice ionic liquid
  - Regular and subregular (metallic liquids and solids)
  - Sublattice (complex solid solutions based on site occupancies)
- Data format

  Fixed-term heat capacity equation = $a+bT+cT^2+d/T^2$
  (Extends up to a 6 additional terms: Variable powers of T)

  Gibbs energy format of 6 fixed-term and 6 extended values

  $$G = A + B\,T + C\,T\ln T + D\,T^2 + E\,T^3 + F/T + G\,T^i + H\,T^j + I\,T^k + J\,T^l + K\,T^m + L\,T^n$$

Progress in *MSTDB* Content Development: Fluoride Systems Status

Pseudo-Binary Systems

	NaF	BeF_2	KF	RbF	CaF_2	ZrF_4	ThF_4	PuF_3	UF_4	UF_3	CsF	CeF_3	LaF_3	SrF_2	MgF_2
LiF	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
NaF		✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
BeF_2						✓	✓	✓	✓						
KF				✓	✓			✓			✓		✓	✓	✓
RbF								✓			✓		✓		
CaF_2							✓						✓	✓	✓
ZrF_4									✓						
ThF_4								✓	✓		✓	✓			
PuF_3									✓		✓		✓		
UF_4										✓					
UF_3															
CsF													✓		
CeF_3															
LaF_3															
SrF_2															✓

✓ In *MSTDB*

✓ In Literature

Pseudo-Ternary Systems in *MSTDB*

- LiF-BeF_2-UF_4
- LiF-BeF_2-ThF_4
- LiF-BeF_2-NaF
- LiF-BeF_2-PuF_3
- LiF-NaF-UF_4
- LiF-ThF_4-PuF_3
- LiF-CaF_2-ThF_4
- LiF-UF_4-PuF_3
- LiF-LaF_3-CsF
- LiF-NaF-LaF_3
- LiF-NaF-RbF
- LiF-NaF-PuF_3
- LiF-CsF-PuF_3
- NaF-BeF_2-ThF_4
- NaF-BeF_2-UF_4
- NaF-BeF_2-PuF_3
- NaF-UF_4-ThF_4
- NaF-KF-CaF_2
- LiF-KF-NaF
- LiF-KF-CsF
- LiF-KF-RbF
- LiF-KF-CaF_2
- LiF-CaF_2-LaF_3
- LiF-CeF_3-ThF_4
- NaF-CaF_2-LaF_3
- BeF_2-UF_4-ThF_4

Remaining in literature

- LiF-MgF_2-CaF_2
- LiF-SrF_2-CaF_2
- NaF-CaF_2-SrF_2
- NaF-MgF_2-CaF_2

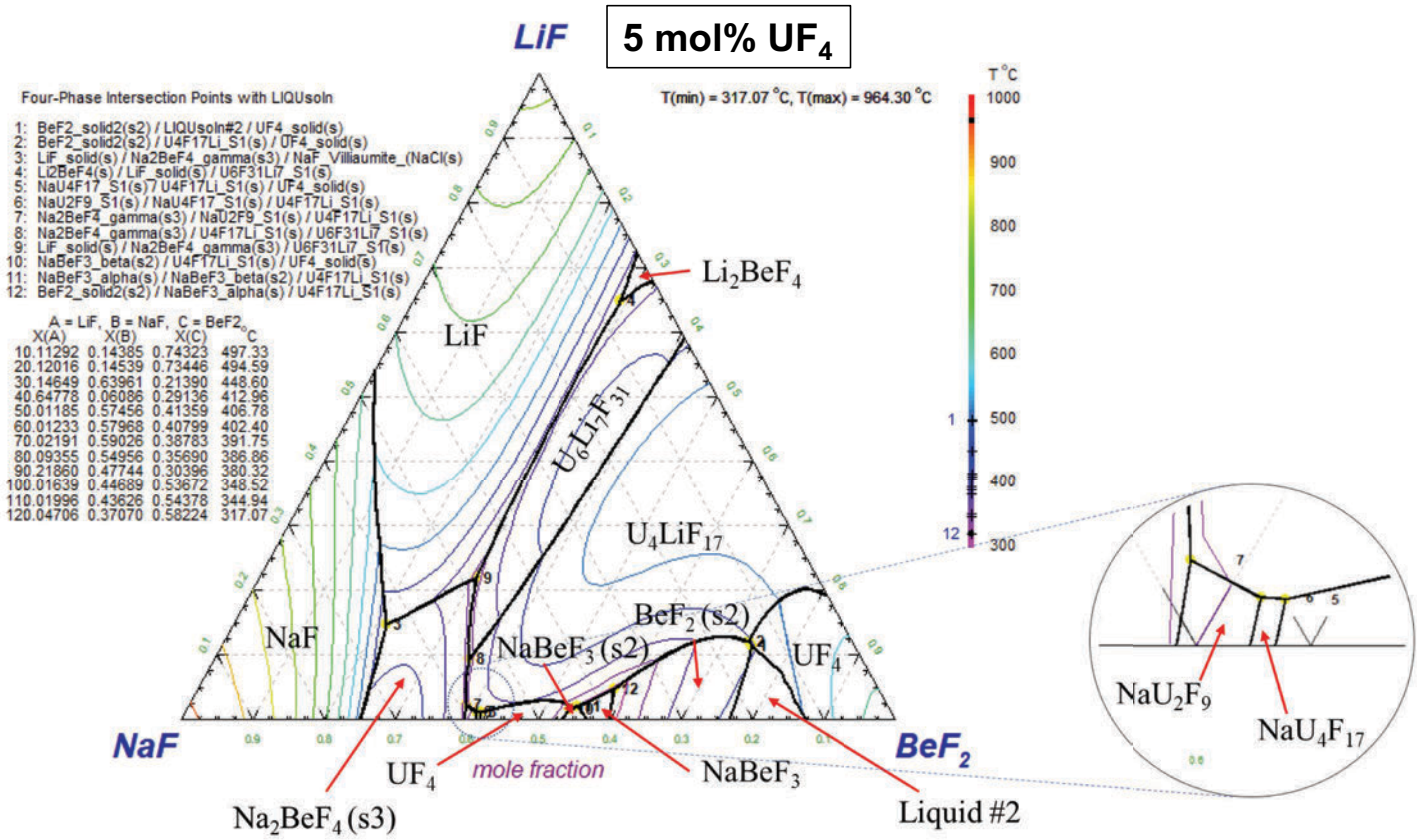
MSTDB Content for Fluoride Systems Available for Use in MSR Modeling and Simulation

- Current components: **LiF-BeF_2-NaF-KF-CaF_2-UF_3-UF_4-ThF_4-PuF_3-RbF-LaF_3-CsF-CeF_3**

While a substantial number of constituents are already incorporated in ***MSTDB***, **not all of their potentially important cross interactions have been modeled – Example: UF_3-UF_4 relations remain unmodeled**

- Where information is available these need to be incorporated
- Where information is incomplete, original experimental/computational work is needed

Complex Fluoride Phase Equilibria Computed From *MSTDB*



Progress in *MSTDB* Content Development: Chloride Systems

All subsystem pseudo-binaries are defined for $NaCl\text{-}MgCl_2\text{-}PuCl_3\text{-}UCl_3$

Pseudo-Binary Systems

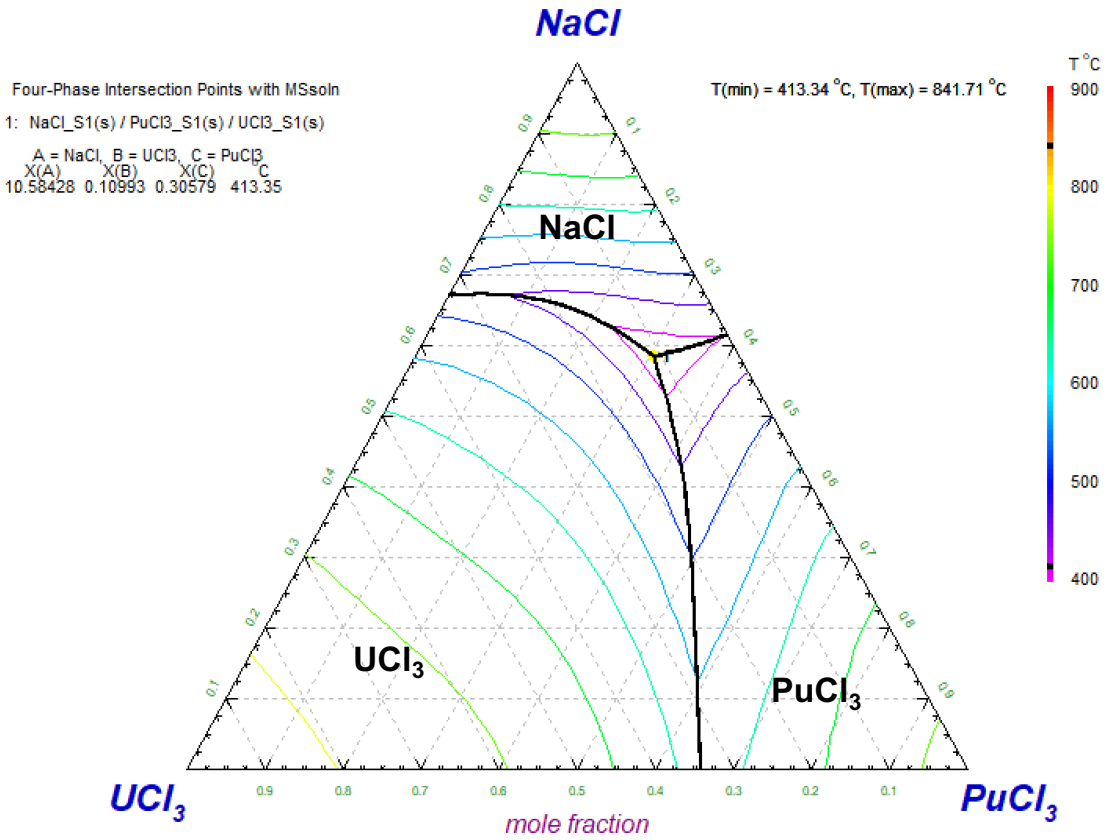
	NaCl	$MgCl_2$	KCl	RbCl	$CaCl_2$	CsCl	$PuCl_3$	UCl_3	$ZnCl_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$	$NiCl_2$	$SrCl_2$
LiCl	✓	✓	✓	✓	✓	✓								✓
NaCl		✓	✓		✓		✓	✓	✓	✓	✓	✓	✓	✓
$MgCl_2$			✓		✓		✓	✓	✓	✓	✓	✓	✓	✓
KCl					✓				✓	✓	✓	✓	✓	✓
RbCl														
$CaCl_2$									✓	✓	✓	✓	✓	✓
CsCl														
$PuCl_3$								✓						
UCl_3														
$ZnCl_2$										✓	✓	✓	✓	
$MnCl_2$											✓	✓	✓	
$FeCl_2$												✓	✓	
$CoCl_2$													✓	
$NiCl_2$														

✓ In *MSTDB*
✓ In Literature

Pseudo-Ternary Systems In Literature

- $NaCl\text{-}KCl\text{-}MgCl_2$
- $NaCl\text{-}KCl\text{-}FeCl_2$
- $NaCl\text{-}MgCl_2\text{-}FeCl_2$
- $NaCl\text{-}MgCl_2\text{-}KCl$
- $NaCl\text{-}RbCl\text{-}CaCl_2$
- $KCl\text{-}CaCl_2\text{-}FeCl_2$
- $NaCl\text{-}CoCl_2\text{-}NiCl_2$
- $LiCl\text{-}KCl\text{-}MgCl_2$
- $LiCl\text{-}KCl\text{-}CaCl_2$
- $LiCl\text{-}NaCl\text{-}CaCl_2$
- $LiCl\text{-}RbCl\text{-}CaCl_2$

Complex Chloride Phase Equilibria Computed From *MSTDB*



MSR Efforts Relate to EURATOM I-NERI

Development of a Thermochemical Database Structure, Models, and Values for Molten Salt Reactors

Participants:

U. S. DOE: **T. M. Besmann**
University of South Carolina

Euratom: **O. Benes and R. Konings**
JRC-Karlsruhe

Collaborating: **J. W. McMurray**
Oak Ridge National Laboratory

Period: Jan. 2018 – Dec. 2021

I-NERI Outcomes that Support DOE MSR Program

- Round robin evaluation of salt thermochemical properties
  - Assure shared data are consistent with sufficient accuracy
  - Identify any issues in measurement techniques/instruments

- JRC-Karlsruhe activities measurements and generated models for subsystems within
  - $NaCl\text{-}MgCl_2\text{-}UCl_3\text{-}PuCl_3$
    - Example: Measurements to sufficiently determine eutectic composition for $NaCl\text{-}UCl_3$
  - $LiF\text{-}ThF_4\text{-}UF_4\text{-}PuF_3$
    - Example: $PuF_3\text{-}ThF_4$ novel experimental data

- Informal access to JRC thermochemical database, *JRCMSD* to support development of the DOE database *MSTDB*

Thermodynamic Modeling Framework and Data

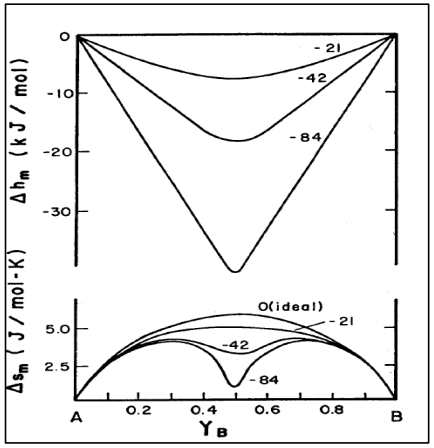
- CALPHAD (CALculation of Phase Diagrams) method
  - Semi-empirical Gibbs energy models based on the physical and chemical properties of represented phases
  - Uses all available validated data generated from experiments or supplied from computation.
    - Models can be extrapolated with high degree of confidence
  - Two sublattice modified quasichemical model (MQM) should be used for the melt
    - Already used extensively within the CALPHAD community for molten salt and other systems
    - JRC-Karlsruhe has substantial experimental data and database for fluoride and chloride systems modeled using the MQM
  - Sublattice models will be used for crystalline phases following Compound Energy Formalism approach
- Significant data needs remain as experimental thermodynamic data is lacking, particularly for chloride systems

MQM Formalism

$$(A-A)+(B-B)=2(A-B);\ \Delta g_{AB}$$

$$G=(n_A g_A^{\circ}+n_B g_B^{\circ})-T\Delta S^{\text{config}}+(n_{AB}/2)\,\Delta g_{AB}$$

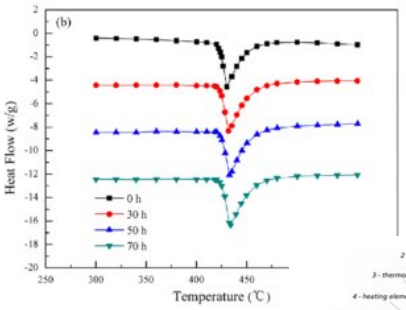
$$\Delta S^{\text{config}}=-\mathrm{R}\,(n_A \ln X_A+n_B \ln X_B)$$
$$-\mathrm{R}\,[n_{AA}\ln(X_{AA}/Y_A^2)+n_{BB}\ln(X_{BB}/Y_B^2)$$
$$+n_{AB}\ln(X_{AB}/2Y_AY_B)]$$

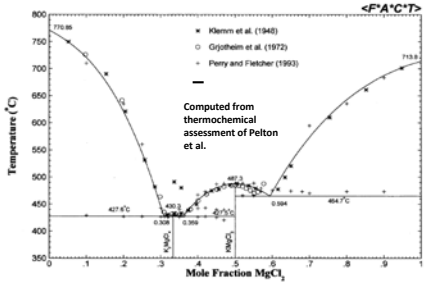


Data from Phase Equilibria and Thermochemical Measurements

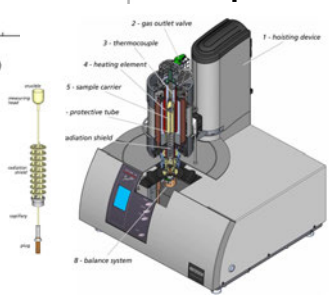
- X-ray diffraction and ceramography of quenched samples
- Thermal analysis methods
  - Differential Scanning Calorimetry (DSC)
  - Differential Temperature Analysis (DTA)
  - Thermogravimetric analysis (TGA)
  - Mass spectrometry (MS)
- Thermochemical data of the form of
  - Phase relations
  - Reaction enthalpies
  - Transition temperatures
  - Vapor pressures

DSC curves of the ternary eutectic chloride salt

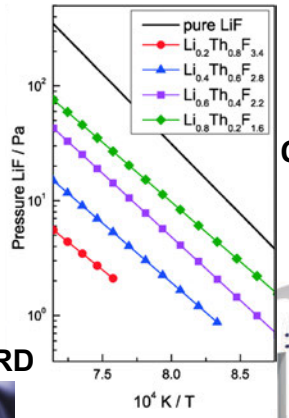




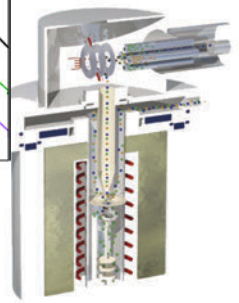
TGA/DSC at multiple labs



Vapor pressure/species

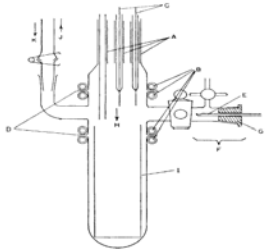


ORNL Skimmer



Electrochemical Cells

Pt | UCl_4-UCl_3; melt || AgCl; melt | Ag(s)
U(s) | UCl_3; melt || AgCl; melt | Ag(s)
U(s) | UCl_3; melt || melt; Cl_2(g) | C(s)
Pt | UCl_4-UCl_3; melt || melt; Cl_2(g) | C(s)

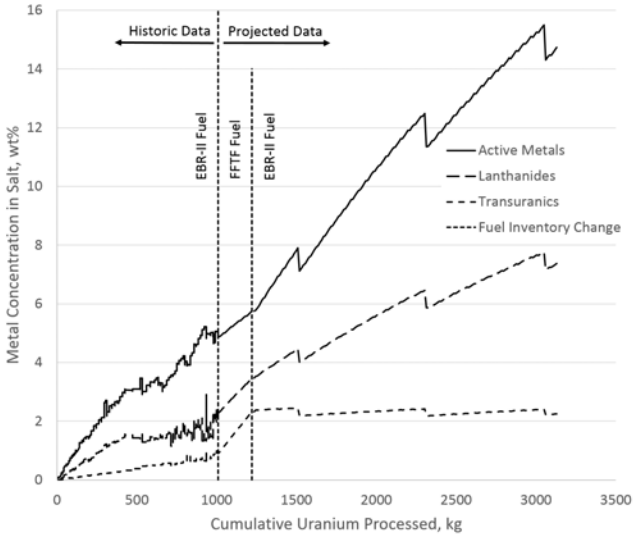


High Temperature XRD

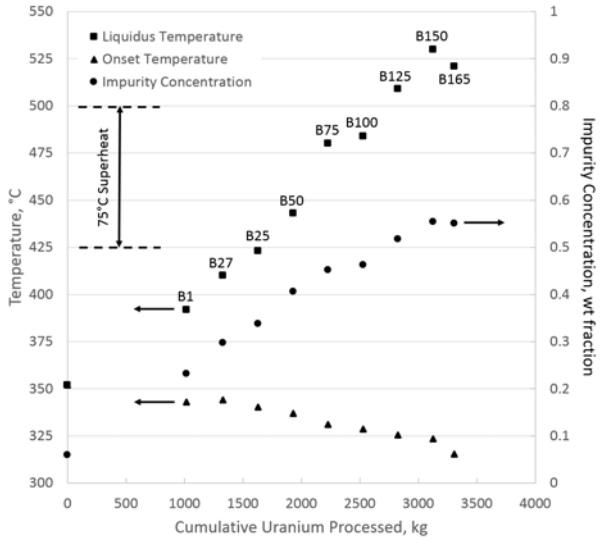
Using Pyroprocessing Simulation Results to Guide Thermochemical Measurements

- Example shown is based on the pyrochemical treatment of used EBR-II and FFTF driver fuels at the INL Fuel Conditioning Facility
- Salt system is within the Mk-IV electrorefiner. It is a LiCl-KCl eutectic salt with actinides and fission product loading.
- The operating temperature is 500°C. Study determined the effect of liquidus temperature of the salt during future processing.

Historical and Simulated Process Modeling

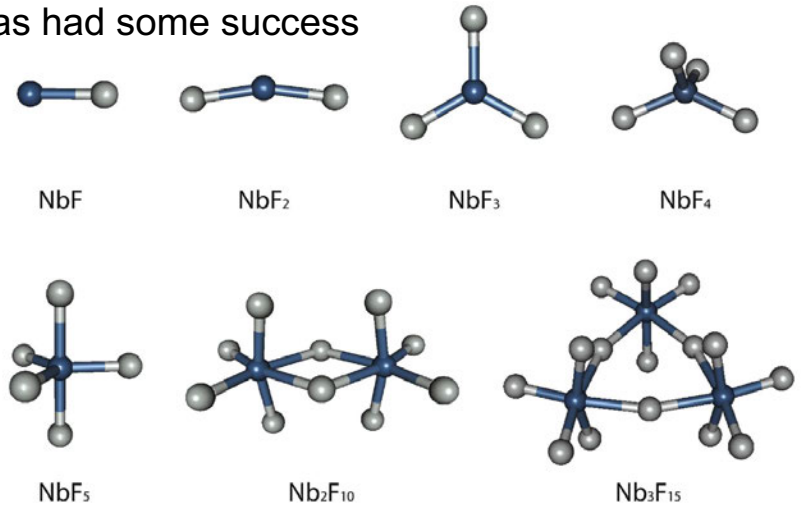


Thermochemical Measurements Of Simulated Salts



Computational Determination of Thermochemical Values

- First-principles calculations performed using density functional theory (DFT) with the Vienna Ab-initio Simulation Package (VASP) code can be valuable for obtaining (0 K) values for crystalline phases
- Vibrational, configurational, and mixing entropies from the phonon density of states calculations provide entropy (finite temperature) behavior
- Obtaining similar values for the melt is a greater challenge for *ab initio* calculations
  - First principles molecular dynamics has had some success



Geometrical configuration of Nb-F gas species using DFT. Capelli and Konings. Journal of Fluorine Chemistry 208 (2018) 55-64

Development of Thermophysical Database Initiated

- Define the functional needs of the salt chemistry database
- Proposed standardized methods and protocols for molten salt property measurements
- Developed framework for thermophysical properties database that identifies activities (FY19) needed to develop and populate database
- Documented findings from literature review on methods and standards for salt properties measurements
- Compiled initial properties database and initiated critical review of data and methods

Example Assessment of Existing Thermophysical Databases

Predictive Model / *Existing Database*	Accurate	Approximate	Information Gap
Accurate	*Density*		*Melting Point* *Vapor Pressure* *Viscosity*
Data Gap: Standard Measurement Method Exist		*Heat Capacity*	
Data Gap: Difficult to Measure			*Thermal Conductivity*

Qualitative assessment of the thermophysical properties database and predictive modeling methods for high temperature coolant salts by Williams et al., 2006 (adapted).

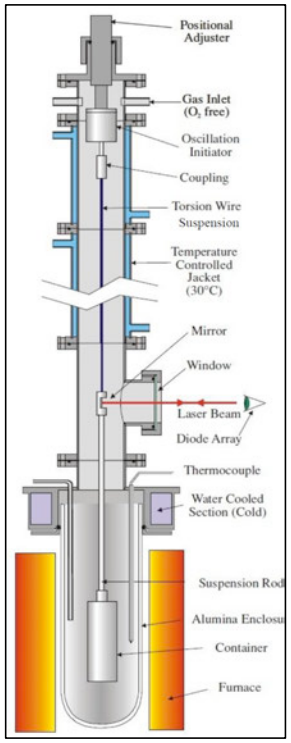
Example Database Table

Salts (mol%)	**MP** (°C)	**BP** (°C)	**Vapor Pressure** (mm Hg)	**Density** (g/cm^3)	**Heat Capacity** (cal/g °C)	**Viscosity** (cP)	**Thermal Conductivity** (W/m K)	**Volumetric expansion** (1/°C)
Alkali Fluorides								
LiF-KF (50-50)								
LiF-RbF (44-56)								
LiF-NaF-KF (46.5-11.5-42)								
LiF-NaF-RbF (42-6-52)								
ZrF_4 Salts								
LiF-ZrF_4 (51-49)								
NaF-ZrF_4 (59.5-40.5)								
RbF-ZrF_4 (58-42)								
LiF-NaF-ZrF_4 (26-37-37)								
BeF_2 Salts								
LiF-BeF_2 (67-33)								
NaF-BeF_2 (57-43)								
LiF-NaF-BeF_2 (31-31-38)								
Chlorides								
LiCl-KCl (59.5-40.5)								
LiCl-RbCl (58-42)								
NaCl-$MgCl_2$ (68-32)								
KCl-$MgCl_2$ (68-32)								
Fluoroborate Salts								
NaF-$NaBF_4$ (8-92)								
KF-KBF_4 (25-75)								
RbF-$RbBF_4$ (31-69)								
MSR Breeder Fuel Salts								
LiF-BeF2-ThF4-UF_4 (73-16-10.7-0.3)								
LiF-BeF2-ThF4-UF_4 (72-21-6.7-0.3)								
LiF-BeF2-ThF4-UF_4 (68-20-11-7-0.3)								
LiF-BeF2-ThF4-UF_4 (63-25-11.7-0.3)								

- Identify and acquire data required to quantify key salt properties.
- Critical review of existing data and identification of gaps for experimental work – *link to standard methods work*.
- Propose standardized methods and protocols for molten salt thermochemical and physical properties measurements.

Example Data Set: Viscosity Li-BeF_2-ThF_4

Method

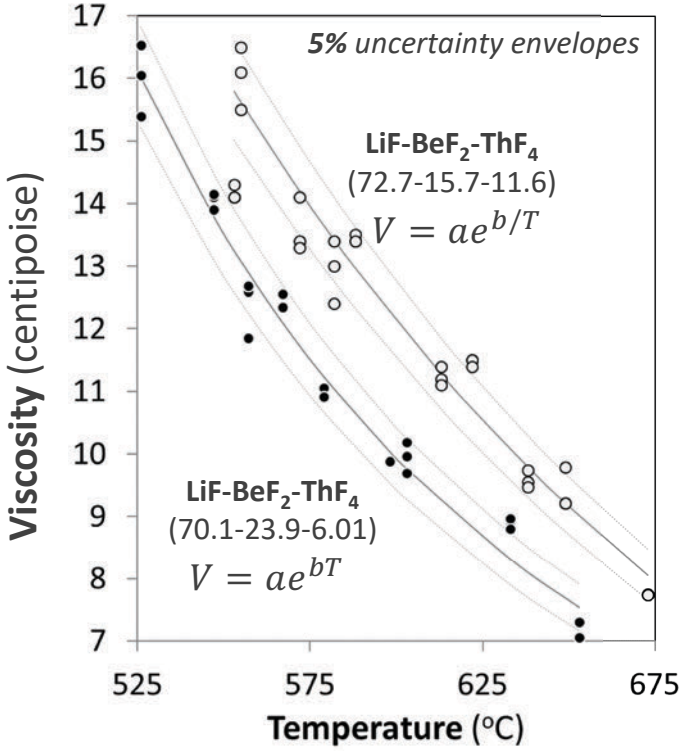


Data tables

LiF	BeF_2	ThF_4	
72.7	15.7	11.6	Mole %
T (°C)	**Visc.1** (cP)	**Visc.2** (cP)	**Visc.3** (cP)
553	14.1	14.3	14.1
555	15.5	16.5	16.1
572	13.4	13.3	14.1
582	12.4	13.4	13
588	13.4	13.5	13.4
613	11.4	11.2	11.1
622	11.5	11.5	11.4
638	9.74	9.56	9.47
649	9.21	9.79	9.22
673	7.74	7.75	7.74

LiF	BeF_2	ThF_4	
70.11	23.88	6.01	Mole %
T (°C)	**Visc.4** (cP)	**Visc.5** (cP)	**Visc.6** (cP)
526	15.39	16.53	16.05
547	14.1	13.9	14.15
557	12.59	12.69	11.85
567	12.35	12.56	12.35
579	11.06	10.92	10.91
598	9.87	9.87	9.88
603	9.69	10.19	9.96
633	8.92	8.97	8.81
653	7.3	7.06	7.06

Correlations/Uncertainties



Examples of relations for representing thermophysical properties – *need experimental validation*

Density	$\rho_{mixture} = \frac{\sum X_i M_i}{\sum X_i V_i(T)}$	Williams et al., 2006
Heat Capacity	$C_p = 33.49 * \frac{\sum X_i N_i}{\sum X_i M_i}$	Williams et al., 2006
Viscosity	$\mu = A\, e^{-\frac{B}{T}}$	Williams et al., 2006
Viscosity	$\mu_{idea\ mixture} = \left[\sum (X_i\ \mu_i^{1/3})\right]^3$	Williams et al., 2006
Thermal Conductivity	$k = 0.119 * \frac{T_m^{0.5}\ v^{0.667}}{(M/n)^{1.167}}$	Cornwell, 1971
Thermal Conductivity	$k = 5.0x10^{-4}T + \frac{32.0}{M} - 0.34$	Ignatiev et al., 2002

$\rho_{mixture}$ - density of the molten salt mixture (g/cm^3), X_i - mole fraction of component i, M_i - molecular weight of component i (g/mole), $V_i(T)$ - molecular volume of component i at temperature T, N_i - number of atoms per salt component i, μ - dynamic viscosity in centipoise (cP), A and B are empirical constants, k - thermal conductivity in watt/m K, T_m - salt mixture melting point in K, v - molar of the salt (cm^3/mol), M - average formula weight of the salt, n - number of ions per salt formula.

Recommendations for Future Activities

- Database: Thermochemical (*MSTDB*) Component
  - Establish thermochemical database with protocols
    - ORNL-hosted website
    - Staff responsible for maintenance and control of data inclusion/modification
    - Board of technical experts provide oversight
    - All potential models/data additions undergo assessment
    - Control of access to database (e.g., open?, as for RSICC?)
  - Prioritized efforts on generating and expanding salt systems
    - Data mining and assessment
    - First principles/data analytics computation
    - Measurements
  - Evolutionary expansion of thermochemical database
    - Can be immediately available
    - Continually accessible with growing content

Recommendations for Future Activities

- Database: Thermophysical Component
  - Select salt compositions to be included in thermophysical database
  - Populate database with critically reviewed data, determine analytical functions for interpolation
  - Determine efficient data format and query structure
  - Identify data gaps
  - Collaborative experimental program to fill data gaps using standard methods and practices
    - Salt compositions
    - Melting Points
    - Density
    - Viscosity
    - Heat Capacity
    - Thermal Conductivity