

Thermophysical Properties Database Development and Supporting Measurements

Anthony Birri, Nicholas Termini, Ryan Chesser, Shane Henderson, Molly Ross, Jacob Numbers, Daniel Orea

Oak Ridge National Laboratory









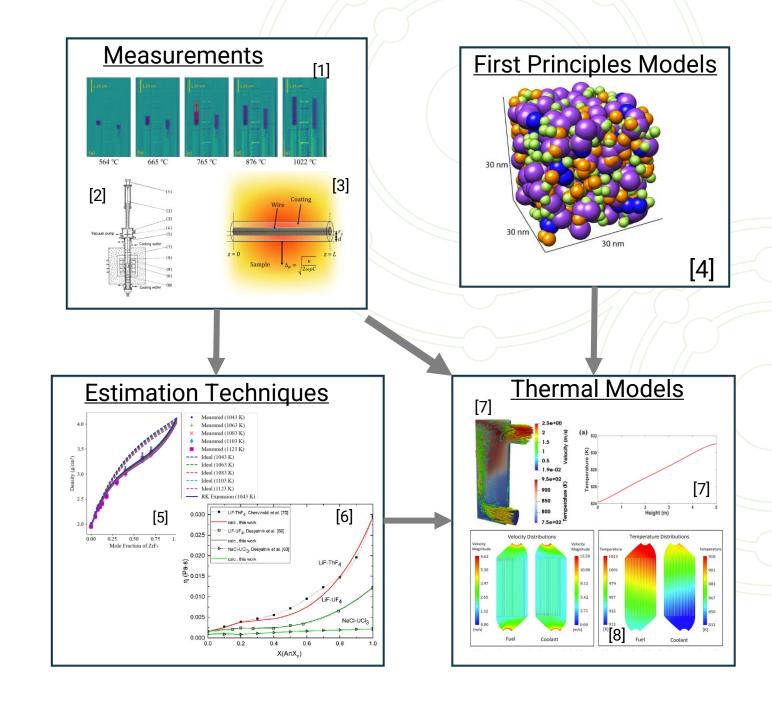






Motivation for Thermophysical Property Characterization

- The design, licensing, and operation of MSRs requires an accurate understanding of fuel and coolant salt thermophysical properties
 - There are a broad range of potential salt mixtures which have potential in MSRs
 - We still have limited understanding of certain properties for certain mixtures
- In order to address this challenge, we need:
 - Experiments to fill critical data gaps and target key mixtures of interest
 - AIMD to understand the relation to molecular structure
 - Predictive models to interpolate and extrapolate for rapid compositional characterization





: 10.1039/F19807602531

10.1021/acs.iced.0c00621

: 10.1038/s42004-022-00684-6

[5]: <u>10.1016/j.ces.2022.117954</u>

[6]: <u>10.1016/j.jnucmat.2022.153536</u> [7]:10.1016/j.nucengdes.2020.110826

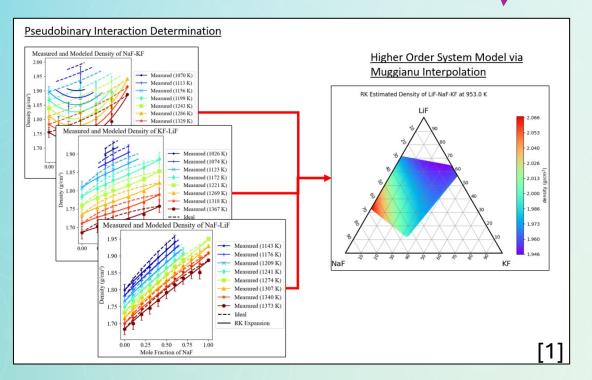
[8]:10.1051/epjn/2019032



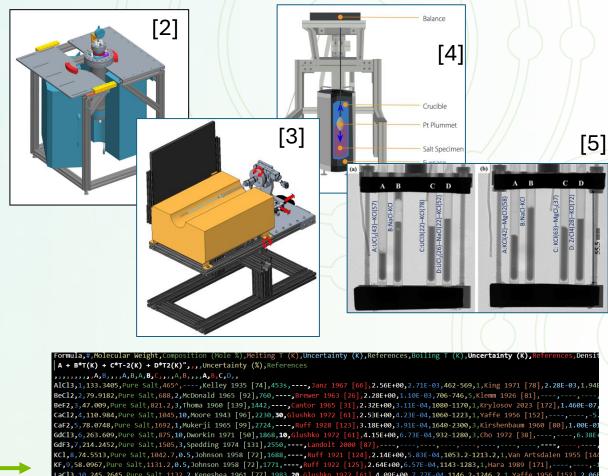


Overview of Thermophysical Characterization Efforts at ORNL

- 1. Experimental Measurements
- 2. Database Development



- [1] ORNL/TM-2023/2955
- [2] Gallagher et. al, J. Chem. Eng. Data 2022, 67, 6, 1406–1414
- [3] Birri et al. (2023). TSEP, 44, 102029.
- [4] ORNL/TM-2020/1633
- [5] Moon et al., Ind. Eng. Chem. Res. 2022, 61, 17665–17673





iF,13,25.9394,Pure Salt,1121.2,1,Douglas 1954 [47],1943,----,R

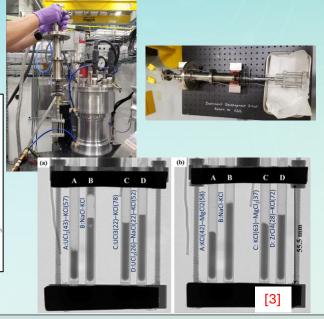


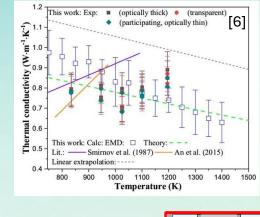
Thermophysical Property Measurement Capabilities at **ORNL**

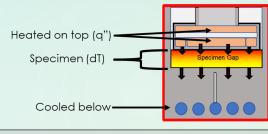
Archimedean Method

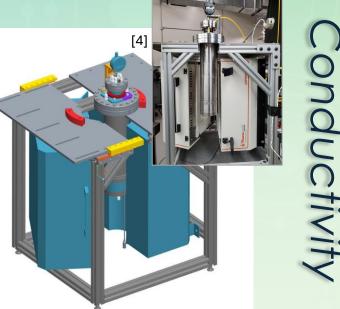




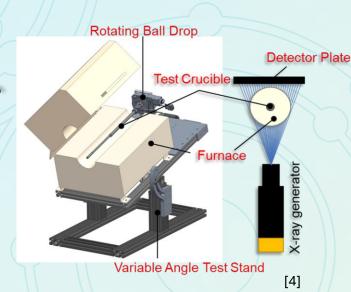


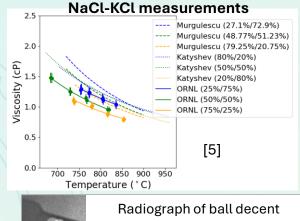


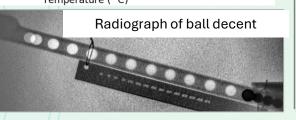


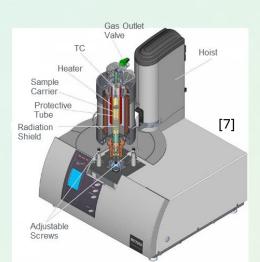


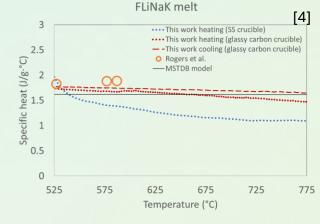














[1] ORNL/TM-2020/1633

[2] Gallagher et. al, J. Chem. Eng. Data 2022, 67, 6, 1406–1414

[3] Moon et al., Ind. Eng. Chem. Res. 2022, 61, 17665–17673

[4] ORNL/TM-2021/2216

[5] ORNL/TM-2023/3048

[6] Gallagher et al., J. Mol. Liq., 2022, 361, 119151

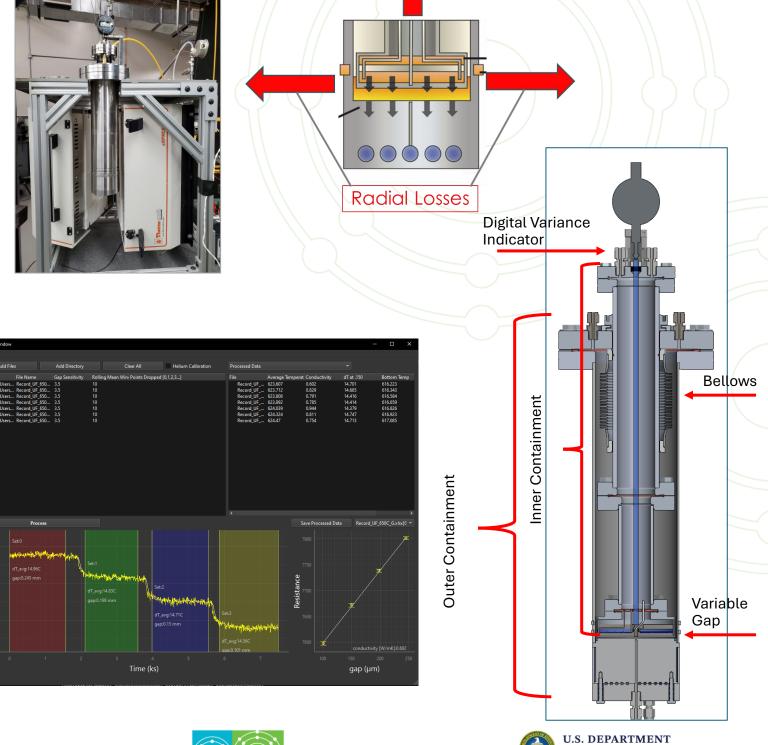
[7] Netzch DSC 404 F3 Pegasus Manual





Variable Gap Thermal Conductivity System Status

- The variable gap system is a direct measurement of thermal conductivity based on driven heat flux through the sample
- Our system is compatible with fluorides, and chlorides, with and without actinides
 - Not currently set up for Be
- Calibration process with He to establish true heat flux versus temperature difference
- Consistently shown good agreement with other experiments and models for various salts
- Automated data processing software, GUI for data analysis



Axial Losses

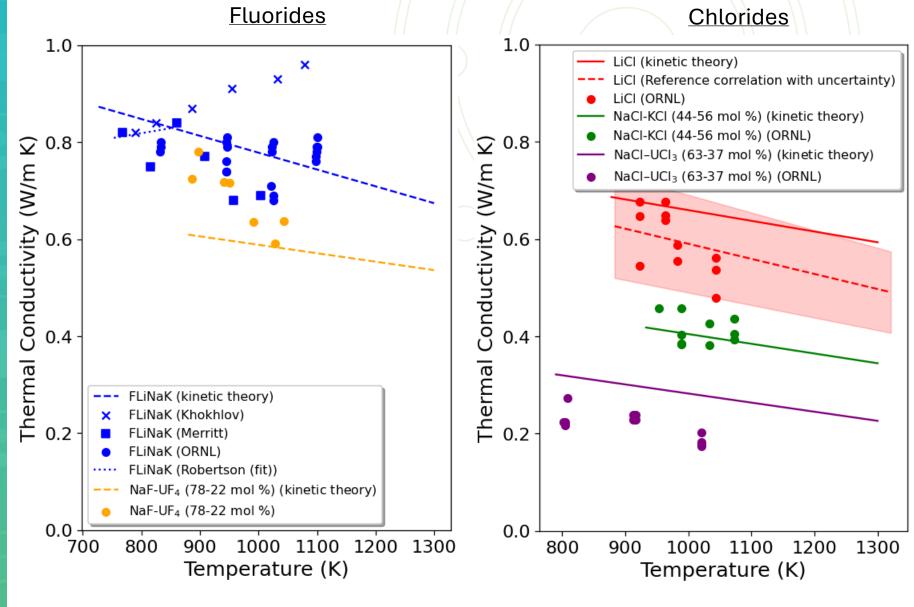




Past and Ongoing Thermal Conductivity Measurements

- We have measured several alkali halide systems:
 - NaCl-KCl (44-56 mol %) [1]
 - FLiNaK [2] (compared against [3,4,5]
 - LiCl [1] for benchmarking with JPCRD
 [6]
- We have also measured actinide halide systems:
 - NaCl-UCl₃ (63-37 mol %) [1]
 - NaF-UF₄
- We are planning to measure soon:
 - NaCl-UCl₃ (63-37 mol %) + surrogate FPs
 - NaF-KF-UF₄

Comparisons of measurements with other studies and theory



[1] ORNL/TM-2024/3650

[2] Gallagher et. al, J. Chem. Eng. Data

(2022). 67(10), 1406–1414

[3] Khokhlov et. al, J. Nuc. Mat. 2011, 410(1-

3), 32—38

[4] Merritt et. al, Int. J. Thermophys. (2022). 43(10).149

[5] Robertson et. al, J. Appl. Phys. (2022). 131(22), 225102

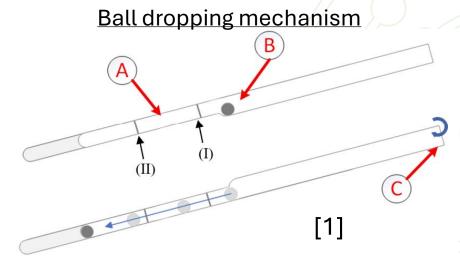
[6] Chliatzou et al. (2018). JPCRD, 47(3), 033104



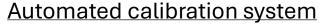


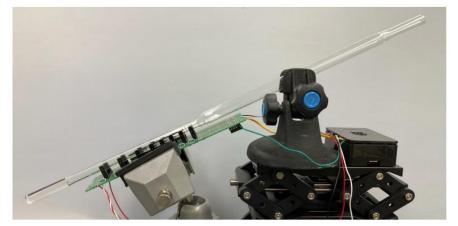
Rolling Ball Viscometer Development Status

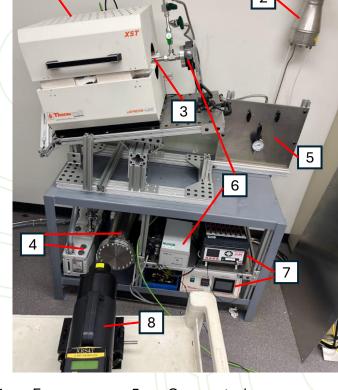
- Based on the terminal velocity of a ball rolling through the molten salt
 - Calibrated with various NIST standard oils and different ball dimensions
- Can make measurements with glass and steel alloys
 - Working to improve accuracy of measurements in steel
- Automated systems for calibration and x-ray triggering
- Our system is compatible with fluorides, and chlorides, with and without actinides



- (A) the measurement section
- (B) The loading section
- (C) Connection to the rotational stage

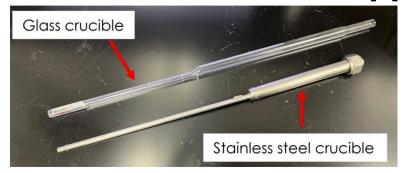






- Furnace
- 2. Ventilation
- Crucible
- 4. Backfill/ pressure maintenance 8. system
- Gas control
- Rotation control Heating/temperature
- control X-ray system (detector

behind furnace [1]







Past and Ongoing Viscosity Measurements

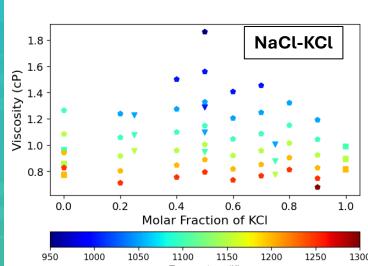
- We have measured several alkali chlorides:
 - LiCl for benchmarking in glass and stainless steel
 - Several system and subsystem measurements of LiCl-KCl-NaCl (compared against [2,3])
- We have also measured NaCl-UCl₃ (compared against [3])
- Planning to measure
 - NaCl-UCl₃ once more
 - NaCl-UCl₃ with surrogate FPs
 - NaF-UF₄

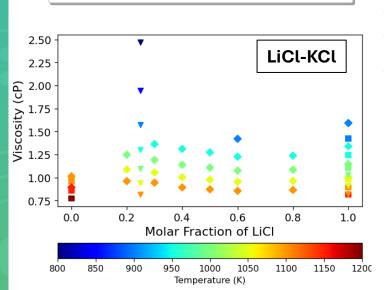
Alkali Chloride Measurements

Katyshev (2001)

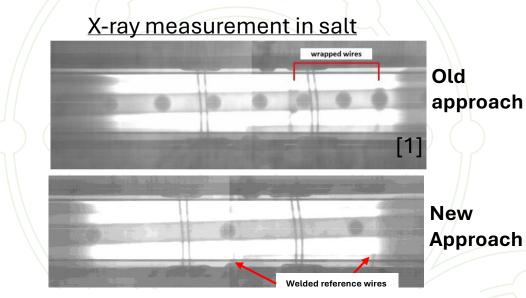
■ Tasiduo (RC, 2019)

Tasiduo (RC, 2019)

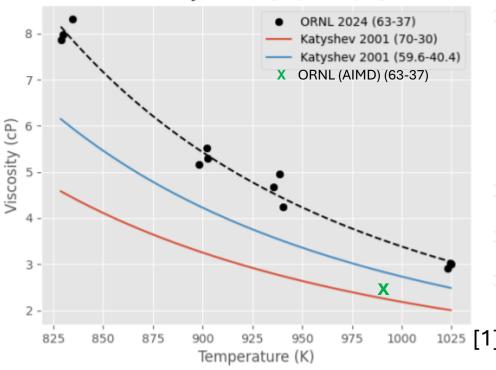




Borcan (1970)



Viscosity of NaCl(63)-UCl3(37)



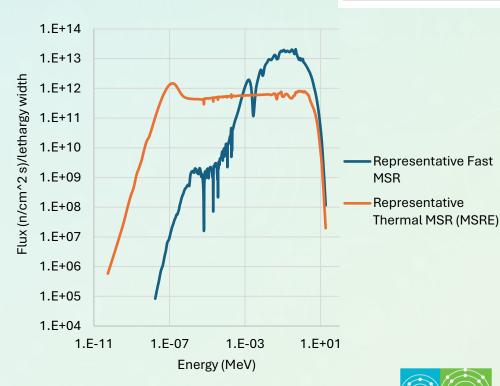


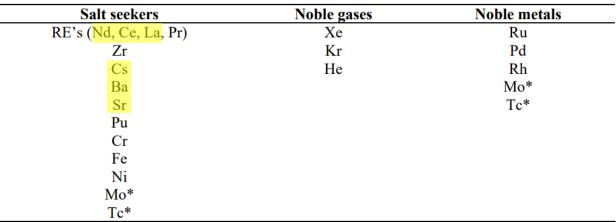


Ongoing Study of Surrogate Fission Products Effect on Transport Properties

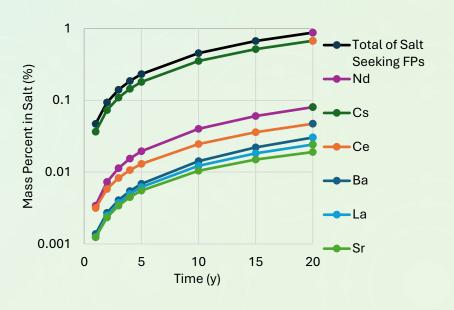
Major FPs [1]

- Need to understand how fission products will affect thermophysical properties
- We are considering a high-burnup case
- Considering NaCl-UCl₃ this FY
 - Simultaneously running calculations for NaF-UF₄
- Can input respective fast/thermal fluxes into ORIGEN to calculate FP inventories
 - Only looking at salt seekers
 - This is a simplified assumption because it ignores removal terms





*Expected to behave as noble metals





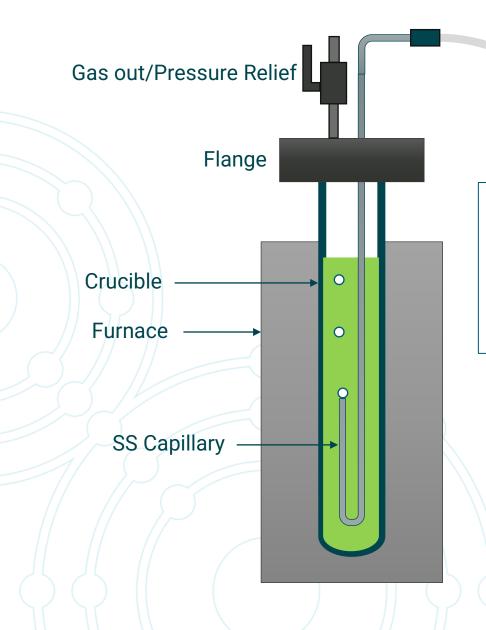
^[2] Wargon et. al (2023). Representative Neutronics Models of MCFR Reactors





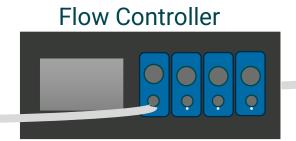
^[3] Hartanto et. al (2024). PHYSOR 2024, 2058-2067

Surface Tension Measurement System Development



5/1/2025

Pressure transducer



P

The surface tension, γ , can be obtained from the measured bubble pressure and radius

$$P_{st} = \frac{2\gamma}{r_{in}}$$

Experimental Plan

- Test system in water Observe bubble formation visually and compare to pressure transducer output.
- 2. Measure surface tension of nitrate and/or chloride salts.
- Measure surface tension of fluoride salts.





Air – Water Capillary: 0.3 mm ID

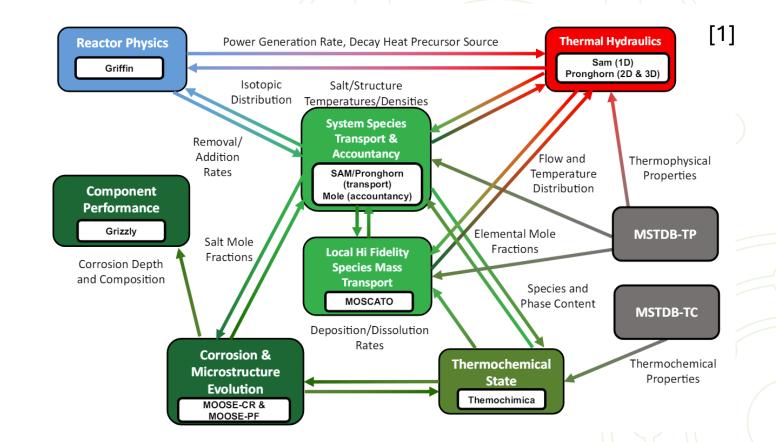


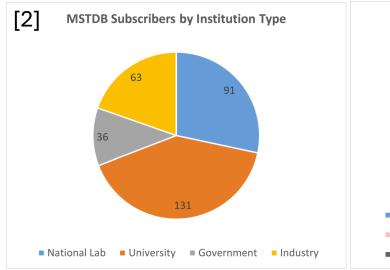


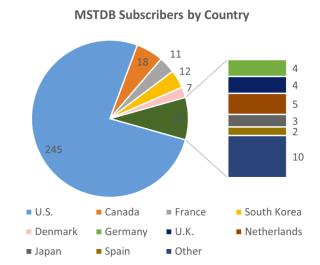
What is MSTDB?

- The Molten Salt Thermal Properties
 Database–Thermochemical (MSTDB-TC) and Molten Salt Thermal Properties Database–Thermophysical (MSTDB-TP) databases are available via the ORNL/ITSD Gitlab Server.
 - MSTDB-TC contains Gibbs energy models and values for molten salt components and related systems of interest with respect to molten salt reactor technology.
 - MSTDB-TP consists of tabulated thermophysical properties and relations for computing properties as a function of temperature or composition.
- MSTDB has >320 users currently













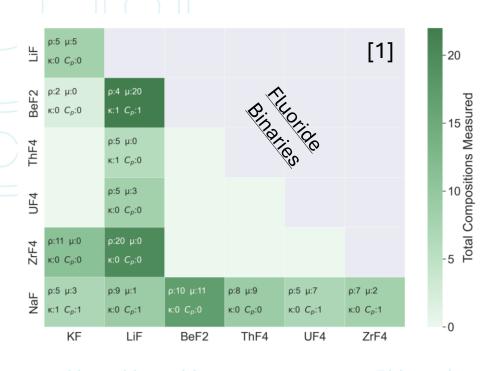


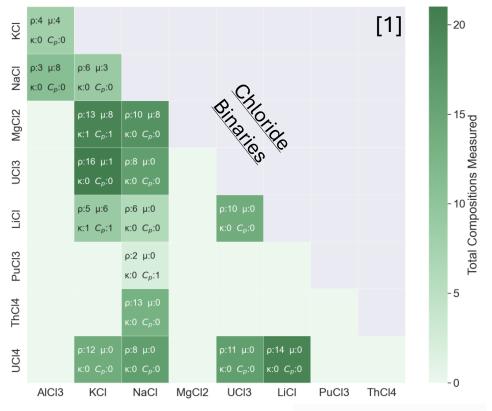
Current State of MSTDB-TP

- As per the current version release (3.1) There are 820 entries, including:
 - 33 pure compounds
 - 380 pseudo-binaries
 - 395 pseudo-ternaries
 - 12 pseudo-quaternaries
- Each property entry in the database includes a margin of experimental error

• This list is constantly expanding. The data is based on the outputs of 180+ independent

experimental studies in literature.





Pure Compounds

Salt	Measurements			
	ρ	μ κ c_p		
AlCl3	1	1	0	1
BeCl2	1	0	0	0
BeF2	1	1	1	1
CaCl2	1	1	1	1
CaF2	1	1	1	1
GdCl3	1	1	0	0
GdF3	0	0	0	0
KCl	1	1	1	1
KF	1	0	1	1
LaCl3	1	1	0	0
LaF3	1	0	0	1
LiCl	1	1	1	1
LiF	1	1	1	1
MgCl2	1	1	1	1
MgF2	1	1	1	0
NaCl	1	1	1	1
NaF	1	0	1	1
NdCl3	1	1	0	0
NdF3	0	0	0	1
NpCl3	0	0	0	0
NpF3	0	0	0	0
PuCl3	0	0	0	1
PuF3	0	0	0	1
SrCl2	1	1	1	0
SrF2	1	1	1	0
ThCl4	1	0	0	0
ThF4	1	0	0	0
UCl3	1	1	0	1
UCl4	1	1	0	0
UF3	0	0	0	1
UF4	1	1	0	1
ZrCl4	1	1	0	0
ZrF4	1	0	0	0

Molten Salt Reactor PROGRAM

<u>Ternaries</u>

Salt	Measurements			
	ρ	μ	κ	c_p
KCl-LiCl-NaCl	4	0	0	0
KCl-LiCl-UCl3	18	0	0	0
KCl-LiCl-UCl4	18	0	0	0
KCl-NaCl-UCl3	18	0	0	0
KCl-UCl3-UCl4	32	0	0	0
AlCl3-LiCl-NaCl	10	10	0	0
LiCl-UCl3-UCl4	21	0	0	0
BeF2-LiF-ThF4	3	2	0	0
BeF2-LiF-ZrF4	1	0	0	0
BeF2-LiF-NaF	5	4	0	5
KF-LiF-NaF	1	1	1	1
LiF-NaF-ZrF4	11	2	2	2
BeF2-LiF-UF4	36	38	2	0
LiF-ThF4-UF4	1	0	0	0
KCl-MgCl2-NaCl	1	1	1	1
LiCl-NaCl-UCl3	18	0	0	0
LiCl-NaCl-UCl4	18	0	0	0
NaCl-UCl3-UCl4	26	0	0	0
BeF2-NaF-UF4	79	71	0	0
BeF2-KF-NaF	1	1	0	1
KF-MgF2-NaF	1	0	1	1
KF-NaF-UF4	3	1	0	2
KF-NaF-ZrF4	1	1	0	1
NaF-UF4-ZrF4	5	4	0	6
RbF-UF4-ZrF4	2	2	0	2

Quaternaries

Salt	Measurements			
	ρ	μ	κ	c_p
BeF2-LiF-ThF4-UF4	1	1	1	1
BeF2-LiF-UF4-ZrF4	1	0	1	0
BeF2-NaF-UF4-ZrF4	1	0	0	0
BeF2-LiF-NaF-UF4	1	1	0	1
KF-LiF-NaF-UF4	2	2	0	2
LiF-NaF-UF4-ZrF4	1	1	0	2
KF-NaF-UF4-ZrF4	0	0	0	2



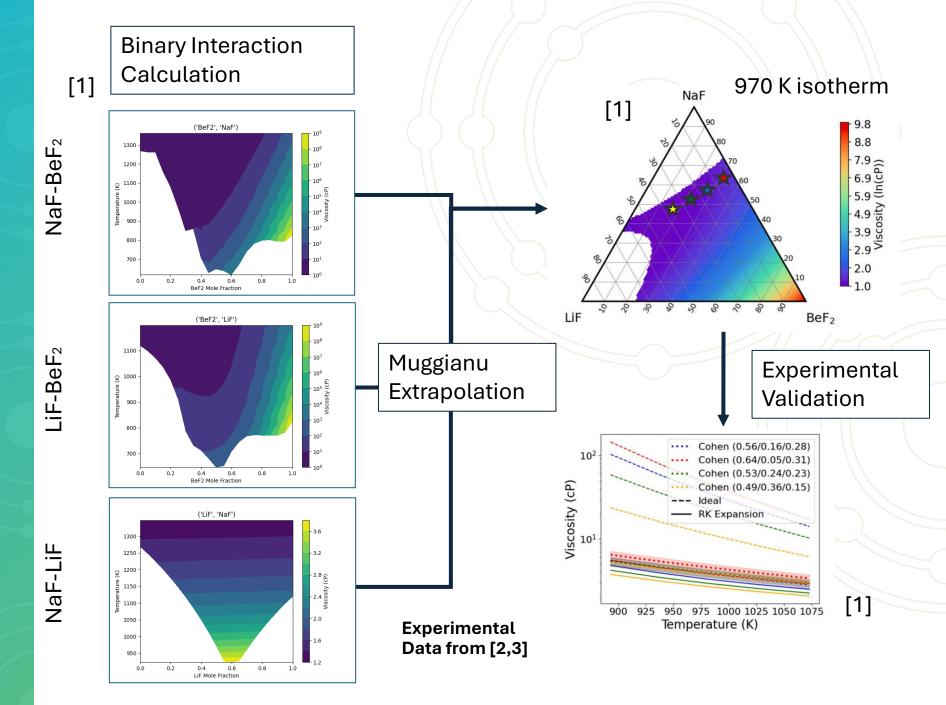
Predictive Modeling with Redlich-Kister

- In order to address gaps in the database, predictive modeling with the RK methodology can yield estimates
 - This method has been developed for density and viscosity [1,4,5]
- This formalism uses experimental data in MSTDB-TP to define non-ideal binary interaction parameters
 - These can be used to interpolate or extrapolate
 - Extensible to arbitrarily sized mixtures
 - Both Saline and the GUI have estimation tools built into them

(2022). Chem. Eng. Sci., 260, 117954.

[1] Birri, A., Termini, N., & Ezell, N. D. B. (2024). *Chem. Eng. Sci.*, 298, 120391.
[2] Blanke, B. C. et al. (1958). MLM-1079
[3] Cohen, S.I., & Jones, T.N. (1957). ORNL-2278.
[4] Agca, C., & McMurray, J. W. (2022). Chem. Eng. Sci., 247, 117086

[5] Birri, A., Gallagher, R., Agca, C., McMurray, J., & Ezell, N. D. B.



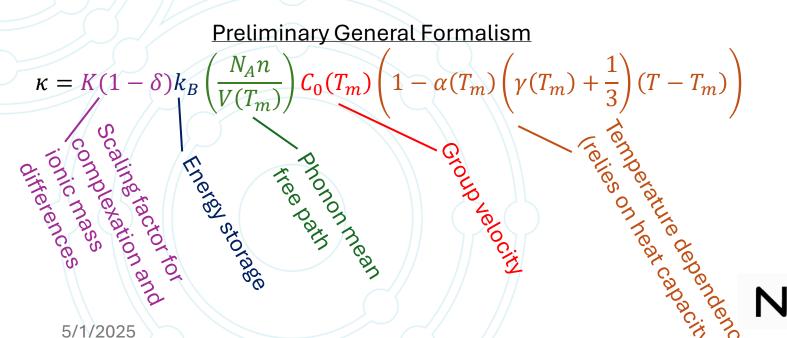


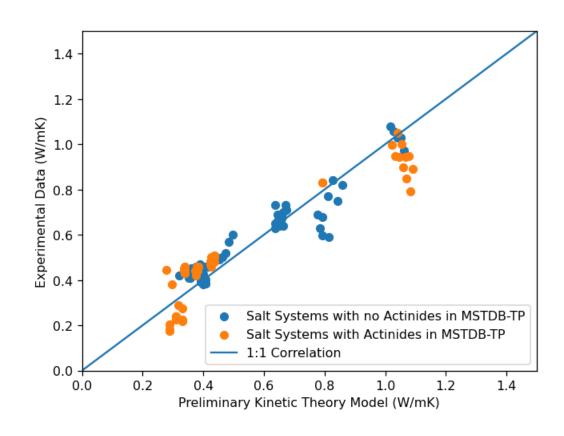




The Difficult Case of Thermal Conductivity Prediction...

- We need a more fundamental model for thermal conductivity prediction
 - Too little data to support RK, many endmembers uncharacterized
- Kinetic theory models have been shown to work well for alkali halides [1,2,3]
 - Modifications to deal with complexation in alkaline earth bearing melts
- Still, actinides are problematic
 - Large molar mass throws off the model
 - Collaborating with BYU to identify a strategy





[1] Gheribi, A. E., Torres, J. A., & Chartrand, P. (2014). Sol.
Energy Mater., 126, 11-25.
[2] Gheribi, A. E. & Chartrand, P. (2016). J. Chem. Phys., 144(8)

[3] Gheribi et al. (2022) Sol. Energy. Mater., 236, 111478





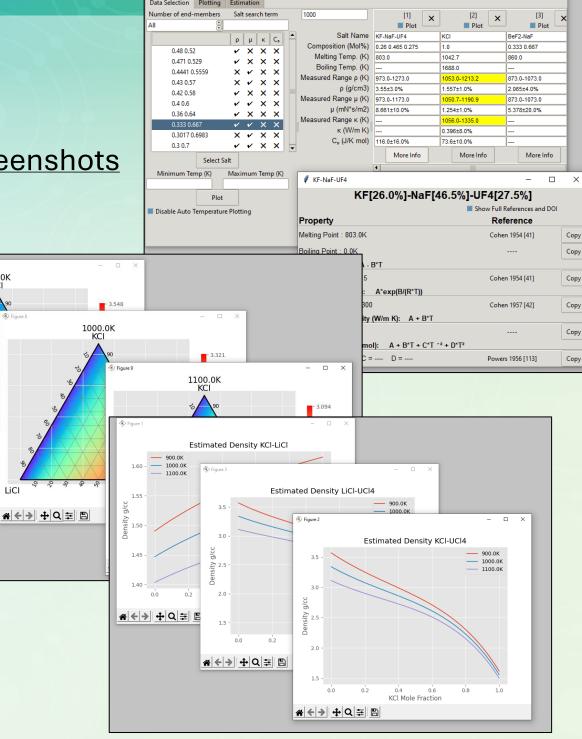
MSTDB-TP User Interfaces

- Saline is the MSTDB-TP API
 - Provides a stable C++ interface for obtaining supported properties (density, viscosity, heat capacity, and thermal conductivity)
 - Designed for integration with other NEAMS codes
- There are two different classes which serve as data models
 - Default: allows for the extraction thermophysical data for compositions in database
 - RK: allows for arbitrary salt mixtures to be estimated
- We also have a GUI which is backed by Saline for more easy access to data

```
Saline API
```

```
#include "default data store.hh
#include "thermophysical_properties.hh"
// Construct the default data store object
Default Data Store d;
// Construct the thermophysical properties object
Thermophysical Properties tp;
// Initialize it with the data store
tp.initialize(&d);
// Pick a composition
tp.setComposition({"LiF","NaF","KF"},{0.465,0.115,0.42});
// Obtain data using temperature in Kelvin
double density = tp.rho(900);
double viscosity= tp.mu(900);
double thermal_conductivity = tp.k(900);
                                                                       [1]
double heat_capacity = tp.cp(900);
```

GUI Screenshots





(-) + Q = B

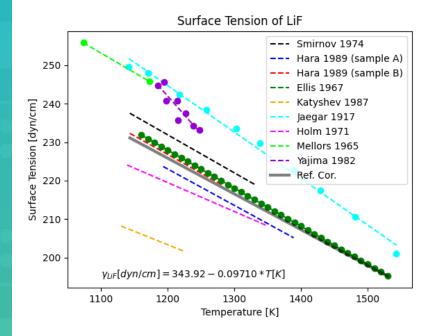


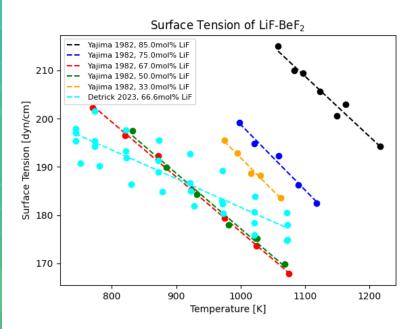


Ongoing Surface Tension Addition Effort

- Collected pure and multicomponent surface tension data for fluorides
 - Chlorides are the current effort
- Evaluated data using ANL quality ranking system
 - This enabled reliable dataset selection
- Follow on effort involves:
 - Reference correlation determinations
 - Development of predictive models

Example data collected:





Pure Component	# Studies	Multi- component	# Studies (# Comps)
LiF	9	LiF-KF	1 (4)
NaF	10	LiF-NaF	1 (1)
KF	5	LiF-BeF ₂	3 (7)
RbF	5	LiF-UF ₄	1 (12)
CsF	4	LiF-ThF ₄	1 (5)
BeF ₂	0	NaF-UF ₄	1 (11)
MgF ₂	4	NaF-KF	1 (1)
CaF ₂	6	NaF-BeF ₂	2 (3)
SrF ₂	3	NaF-ZrF ₄	1 (5)
BaF ₂	4	NaF-NaBF ₄	1 (1)
ZrF ₄	2	KF-BeF ₂	1 (9)
LaF ₃	0	LiF-NaF-KF	4 (1)
ThF ₄	1	LiF-NaF-CaF ₂	1 (1)
UF ₃	0	LiF-NaF-ZrF ₄	1 (11)
UF ₄	1	LiF-KF-ZrF ₄	1 (10)
UF ₆	1	LiF-BeF ₂ -UF ₄	1 (1)
		LiF-BeF ₂ -ThF ₄	2 (49)
		NaF-BeF ₂ -UF ₄	1 (1)
		NaF-ZrF ₄ -UF ₄	1 (1)
		LiF-BeF ₂ -UF ₄ - ThF ₄	2 (33)
		NaF-BeF ₂ - UF ₄ -ThF ₄	2 (33)





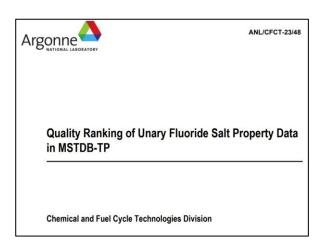


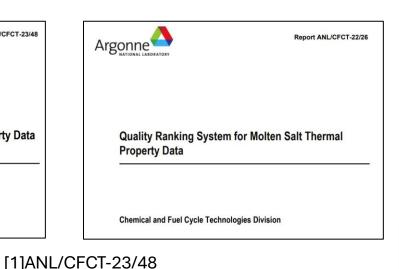
MSTDB-TP Quality Rankings Collaboration

- ANL has put out two reports [1,2] on the QA process for MSTDB-TP
 - One detailing how the rankings work
 - Another on application to pure fluoride compounds for density and viscosity

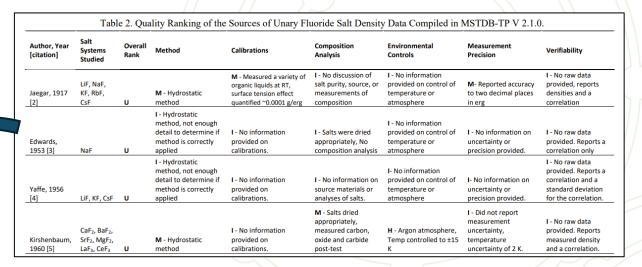
[2]ANL/CFCT-22/26

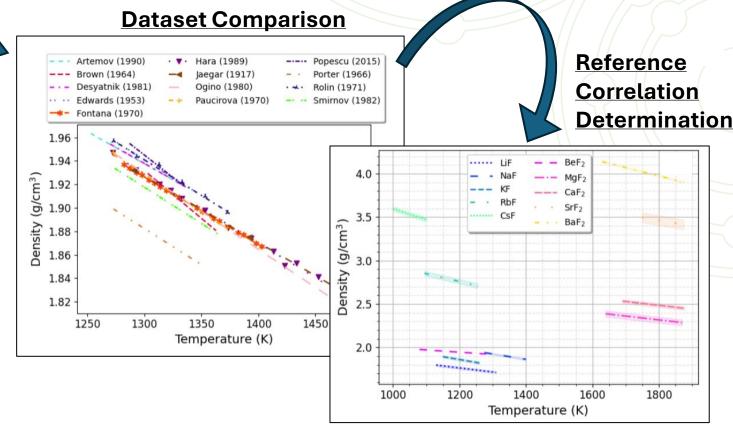
- The MSTDB-TP incorporates quality rankings into the dataset selection and uncertainty characterization as updates are generated
- A continuation of this effort has enabled reference correlation determinations for fluoride density and viscosity
 - Journal manuscript in review for JPCRD





Quality Rankings











Summary

- ORNL is striving to meet the challenge of thermophysical property characterization for MSR relevant salts with a multi-pronged approach
- Experimentally, we are focused on performing transport property measurements, primarily on actinide-bearing salts
 - We are also studying the effect of surrogate FPs
- From a modelling standpoint, we are developing predicative models for rapid characterization of many salts, informed by experimental measurements
- We are collecting and assessing, as exhaustively as we can, thermophysical property data to compile into MSTDB-TP

Acknowledgements

- Ted Besmann and Juliano Shorne-Pinto at USC for collaboration between TC and TP
- Melissa Rose at ANL for quality rankings collaboration
- Joanna McFarlane and Kevin Robb for their molten salt expertise which has better informed decisions made in this work
- Vanda Glezakou and Brett Smith for collaboration regarding AIMD and experimental coordination
- Jacob Numbers and Troy Munro at BYU for collaboration on thermal conductivity prediction
- Brandon Wilson and Donny Hartanto for performing neutronics/depletion calculations

This work is directly funded by the Molten Salt Reactor Campaign and the Nuclear Energy Advanced Modeling and Simulation Program under the Department of Energy, Office of Nuclear Energy.







Thank you

birriah@ornl.gov

