

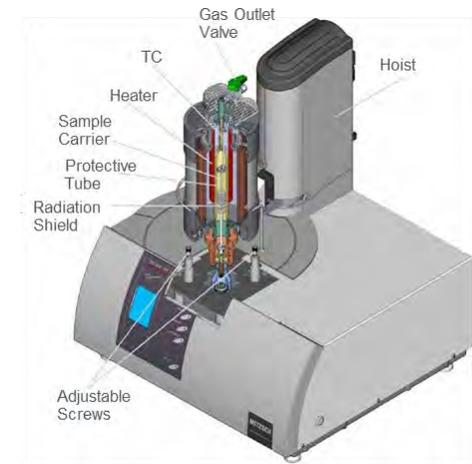
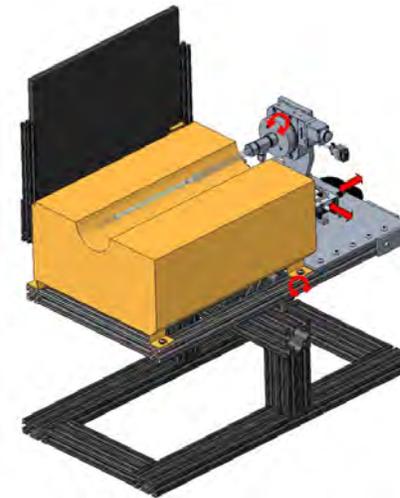
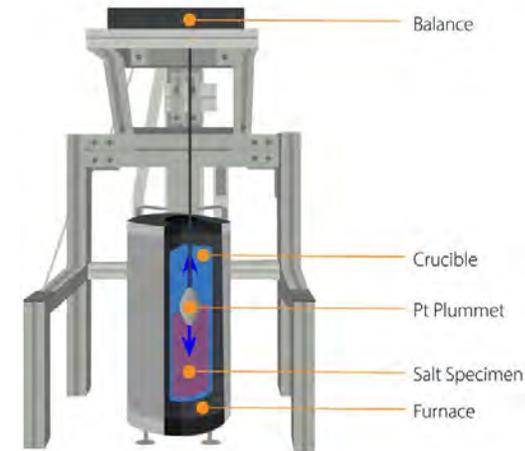
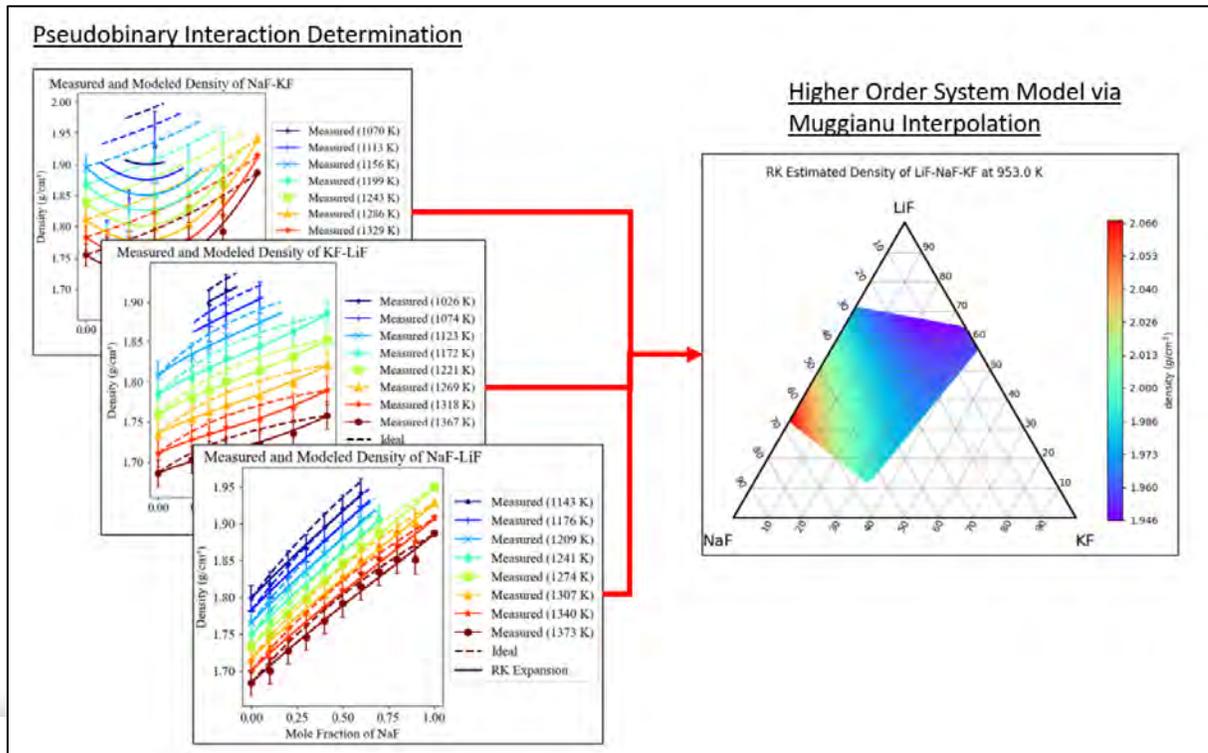


Overview of MSTDB-TP 3.0: Current Status, Future Direction

Anthony Birri, Nicholas Termini, Shane Henderson, Ryan Chesser,
Jacob Numbers, Kevin Garland, N. Dianne Bull Ezell

Overview of Thermophysical Characterization Efforts at ORNL

1. Experimental Measurements
2. Predictive Modeling
3. Database Development



MSTDB-TP v3.0

- The Molten Salt Thermal Properties Database–Thermophysical (MSTDB-TP) contains empirical relations for the following properties:

- Melting and boiling points
- Density
- Viscosity
- Heat Capacity
- Thermal Conductivity

- As per the current version release (3.0) There are **799 entries**, including:

- 33 pure compounds
- 375 pseudo-binaries
- 382 pseudo-ternaries
- 9 pseudo-quaternaries

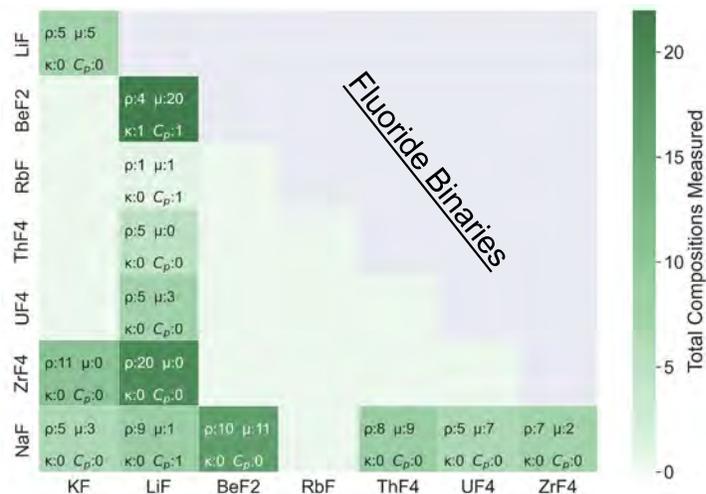
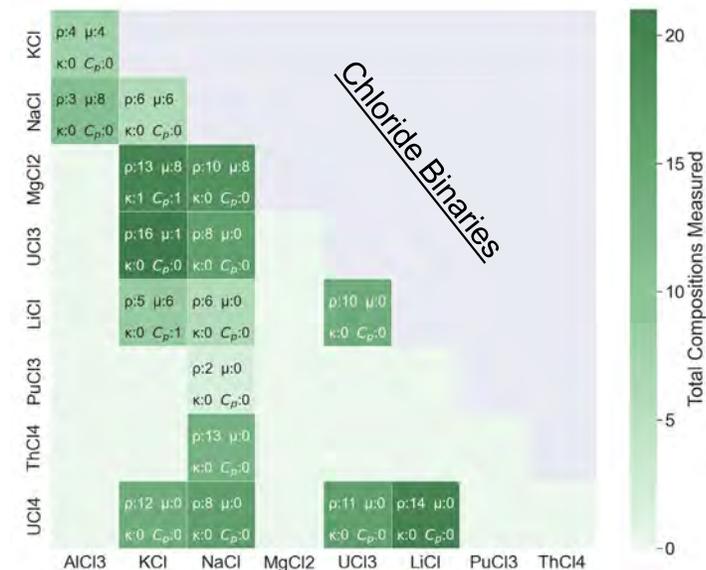
- Each property entry in the database includes a margin of experimental error

- Determined on a case-by-case basis
- This list is constantly expanding. The data is based on the outputs of 170+ independent experimental studies in literature.

- This is one of two arms of MSTDB; MSTDB-TC contains thermochemical properties

Pure Compounds

Salt	Measurements			
	ρ	μ	κ	c_p
AlCl ₃	1	1	0	1
BeCl ₂	1	0	0	0
BeF ₂	1	1	1	1
CaCl ₂	1	1	1	1
CaF ₂	1	1	1	1
GdCl ₃	1	1	0	0
GdF ₃	0	0	0	0
KCl	1	1	1	1
KF	1	1	1	1
LaCl ₃	1	1	0	0
LaF ₃	1	0	0	1
LiCl	1	1	1	1
LiF	1	1	1	1
MgCl ₂	1	1	1	1
MgF ₂	1	1	1	0
NaCl	1	1	1	1
NaF	1	1	1	1
NdCl ₃	1	1	0	0
NdF ₃	0	0	0	1
NpCl ₃	0	0	0	0
NpF ₃	0	0	0	0
PuCl ₃	0	0	0	1
PuF ₃	0	0	0	1
SrCl ₂	1	1	1	0
SrF ₂	1	1	1	0
ThCl ₄	1	0	0	0
ThF ₄	1	0	0	0
UCl ₃	1	0	0	1
UCl ₄	1	0	0	0
UF ₃	0	0	0	1
UF ₄	1	1	0	1
ZrCl ₄	1	1	0	0
ZrF ₄	1	0	0	0



Ternaries

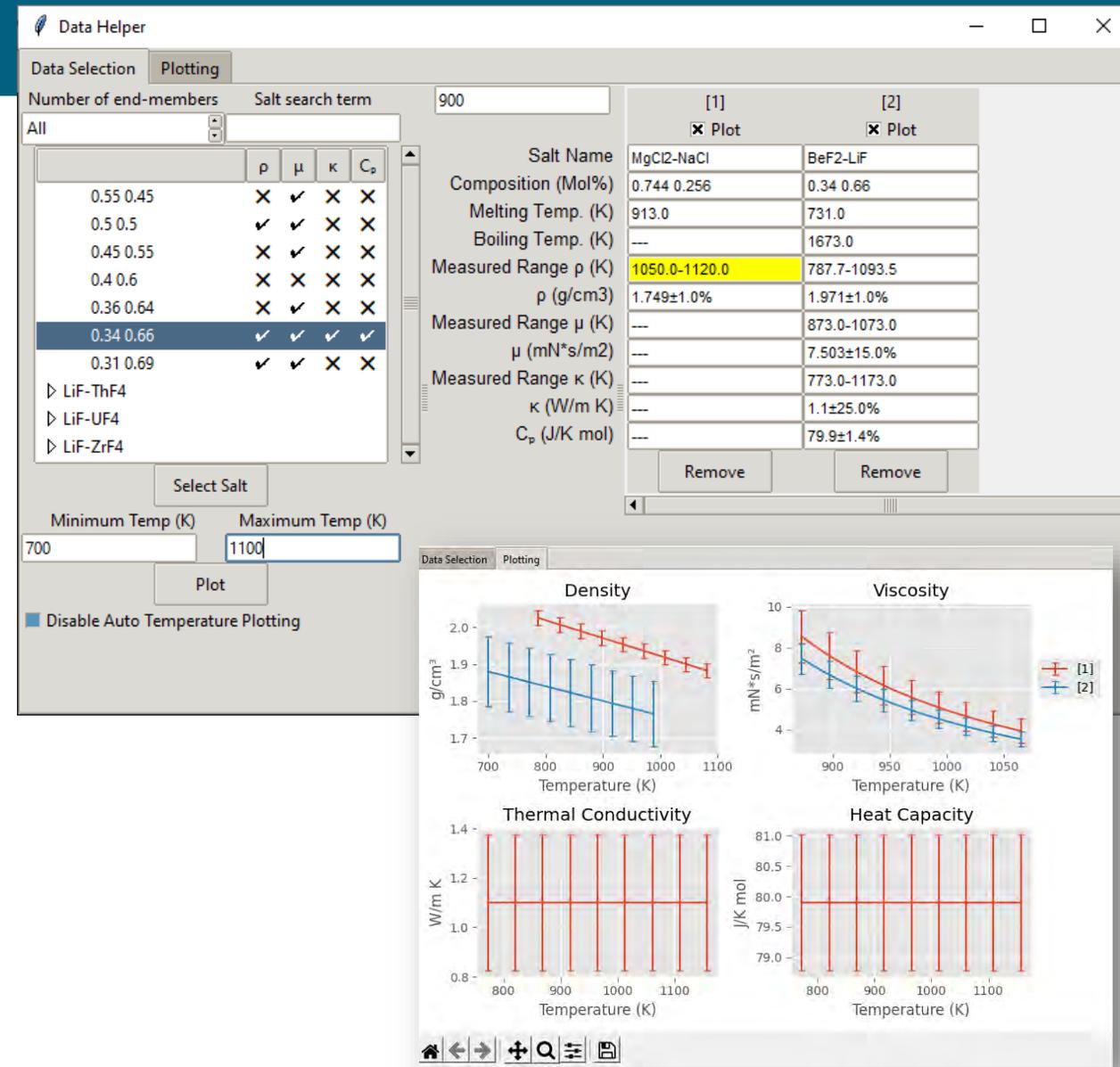
Salt	Measurements			
	ρ	μ	κ	c_p
KCl-LiCl-NaCl	4	0	0	0
KCl-LiCl-UCl ₃	18	0	0	0
KCl-LiCl-UCl ₄	18	0	0	0
KCl-NaCl-UCl ₃	18	0	0	0
KCl-UCl ₃ -UCl ₄	32	0	0	0
AlCl ₃ -LiCl-NaCl	10	10	0	0
LiCl-UCl ₃ -UCl ₄	21	0	0	0
BeF ₂ -LiF-ThF ₄	3	2	0	0
BeF ₂ -LiF-ZrF ₄	1	0	0	0
BeF ₂ -LiF-NaF	5	5	0	0
KF-LiF-NaF	1	1	1	1
BeF ₂ -LiF-UF ₄	36	36	0	0
LiF-ThF ₄ -UF ₄	1	0	0	0
LiCl-NaCl-UCl ₃	18	0	0	0
LiCl-NaCl-UCl ₄	18	0	0	0
NaCl-UCl ₃ -UCl ₄	26	0	0	0
BeF ₂ -NaF-UF ₄	79	71	0	0
BeF ₂ -KF-NaF	1	1	0	0
KF-MgCl ₂ -NaF	1	0	0	0
KF-NaF-UF ₄	2	1	0	1
KF-NaF-ZrF ₄	1	1	0	0
LiF-NaF-ZrF ₄	9	0	0	0
NaF-UF ₄ -ZrF ₄	5	3	0	3
RbF-UF ₄ -ZrF ₄	2	2	0	1

Quaternaries

Salt	Measurements			
	ρ	μ	κ	c_p
BeF ₂ -LiF-ThF ₄ -UF ₄	1	1	1	0
BeF ₂ -LiF-UF ₄ -ZrF ₄	1	0	1	0
BeF ₂ -NaF-UF ₄ -ZrF ₄	1	0	0	0
BeF ₂ -LiF-NaF-UF ₄	1	1	0	0
KF-LiF-NaF-UF ₄	2	2	0	1
LiF-NaF-UF ₄ -ZrF ₄	1	1	0	1

MSTDB-TP Tools

- MSTDB-TP is a large, difficult to navigate .csv file
- 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
- The MSTDB-TP GUI allows for easier navigation and visualization of the data
 - Can provide access to beta version, official GitLab deployment coming soon
- GUI Contact: Nick Termini termininc@ornl.gov
- Saline Contact: Shane Henderson hendersonsc@ornl.gov



Redlich-Kister Modeling Efforts

- Semi-empirical solution model which can be used to predict thermophysical properties
 - Fed data from MSTDB-TP
 - Used to interpolate/extrapolate over compositional/temperature domain of the salt matrix
- Motivation: We can only make measurements across the national laboratories so fast
 - Limited time and funding
 - There are countless possible pseudo-ternary+ systems which may be of interest
- We have established this capability for density
 - 2 peer-reviewed publications, RK parameters in the Gitlab project
- Journal publication in review to demonstrate for viscosity
 - Preliminary results have been disseminated in report: ORNL/TM-2023/2955

Density Efforts

[1] Chemical Engineering Science 247 (2022) 117086

Contents lists available at ScienceDirect

Chemical Engineering Science

Journal homepage: www.elsevier.com/locate/ces

Empirical estimation of densities in NaCl-KCl-UCl₃ and NaCl-KCl-YCl₃ molten salts using Redlich-Kister expansion

Can Agca^a, Jake W. McMurray^b

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

HIGHLIGHTS

- Density of NaCl-KCl, NaCl-YCl₃, KCl-YCl₃, NaCl-UCl₃, and KCl-UCl₃ molten salts were modeled.
- Temperature and composition dependent Redlich-Kister expansion is used in the model.
- NaCl-KCl-UCl₃ and NaCl-KCl-YCl₃ molten salt densities were successfully estimated.
- Muggianu interpolation scheme was used to estimate the ternary molten salt densities.

GRAPHICAL ABSTRACT

Discrepancy

[2] Chemical Engineering Science 260 (2022) 117954

Contents lists available at ScienceDirect

Chemical Engineering Science

Journal homepage: www.elsevier.com/locate/ces

Application of the Redlich-Kister expansion for estimating the density of molten fluoride pseudo-ternary salt systems of nuclear industry interest^a

Anthony Birri^{a,*}, Ryan Gallagher^a, Can Agca^b, Jake McMurray^b, N. Dianne Bull Ezell^b

^aNuclear Energy and Fuel Cycle Division, Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37830, USA
^bMaterials Science and Technology Division, Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37830, USA

HIGHLIGHTS

- Several molten fluoride pseudo-ternary salt system densities were estimated.
- The estimation is based on Redlich-Kister expansion and Muggianu interpolation.
- This method generally outperforms estimation by additive molar volumes.
- Some unmeasured pseudo-binary system densities were also estimated.

[1] Agca, C., & McMurray, J. W. (2022). *Chem. Eng. Sci.*, 247, 117086.

[2] Birri, A., Gallagher, R., Agca, C., McMurray, J., & Ezell, N. D. B. (2022). *Chem. Eng. Sci.*, 260, 117954.

Viscosity Efforts

ORNL/TM-2023/2955

An Overview of the Molten Salt Thermal Properties Database—Thermophysical, Version 2.1.1 (MSTDB-TP v.2.1.1)

Nick Termini
Anthony Birri
Shane Henderson
N. Dianne Bull Ezell

July 2023

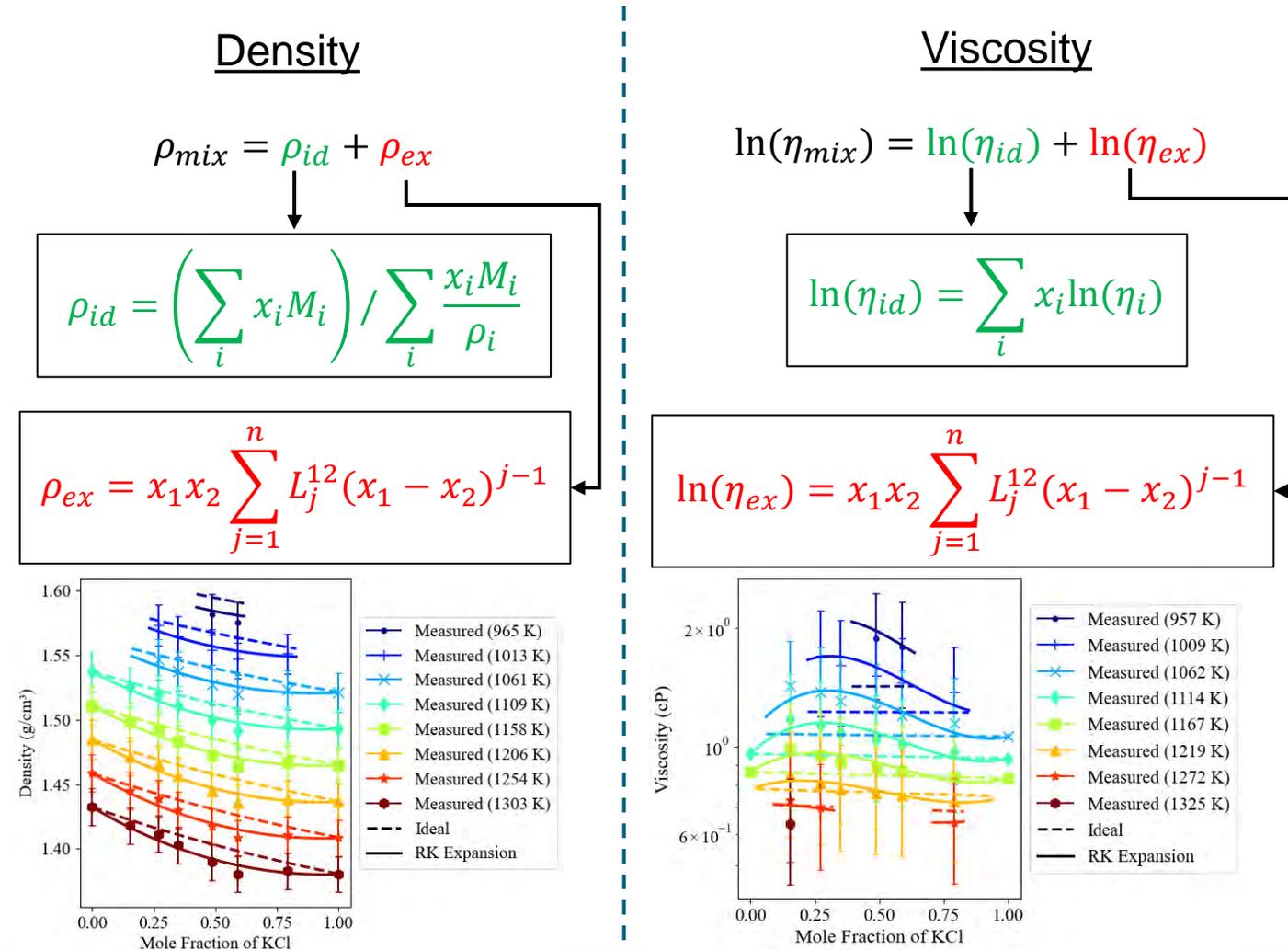
NaF-BeF₂

LiCl-KCl

How RK Modeling Works

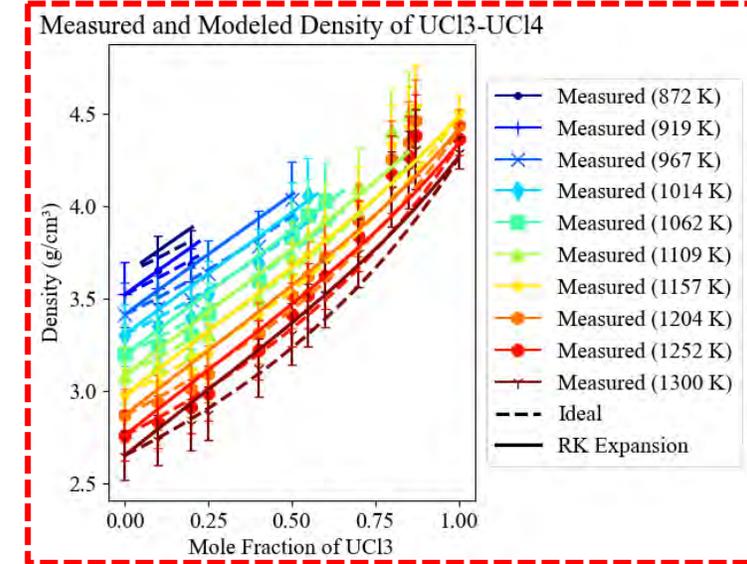
- Based on a combination of ideal and non-ideal components
 - Ideal term depends on the property (e.g. additive molar volumes for density)
 - Informed by pure compound data
 - Non-ideal term follows a specific structure
 - Informed by binary system data
 - RK polynomial for binary systems
 - Muggianu extrapolation for higher order systems (based on RK)
- The non-ideal term is determined through regression techniques
 - The order of the fit is property/salt dependent
 - Some properties/salts exhibit highly non-linear non-ideal mixing

Pseudo-binary RK example: KCl-NaCl



Current Status of Redlich-Kister Density Modeling

- Formalism has been shown to increase accuracy in property estimation versus ideal models
 - This has been shown for both chlorides and fluorides
- RK parameters are available on the GitLab project
- RK parameters can be input into Saline for property estimation of arbitrary salt mixtures
 - Assumes ideal mixing if pseudo-binary data unavailable



Accuracy improvements from RK modeling

Statistical measurands for fits to determine binary interaction parameters in Table 4.

System	R^2 (ideal)	R^2 (RK expan.)	ϵ_{avg} (ideal)	ϵ_{avg} (RK expan.)	ϵ_{max} (ideal)	ϵ_{max} (RK expan.)
NaF-LiF	0.96	0.995	0.59%	0.18%	0.89%	0.56%
NaF-KF	0.58	0.71	1.2%	1.0%	5.9%	5.3%
NaF-ZrF ₄	0.84	0.997	5.4%	0.69%	9.6%	1.8%
LiF-ZrF ₄	0.68	0.994	7.8%	1.1%	18.4%	7.8%
NaF-BeF ₂	0.77	0.94	1.5%	0.67%	5.5%	4.4%
LiF-BeF ₂	0.75	0.997	1.5%	0.15%	3.9%	0.59%
LiF-ThF ₄	0.998	0.9992	0.89%	0.70%	2.3%	1.9%
NaF-ThF ₄	0.98	0.9997	3.0%	0.30%	5.9%	1.2%
NaF-UF ₄	0.97	0.995	3.6%	1.2%	10.4%	4.5%

from:

Birri, A., Gallagher, R., Agca, C., McMurray, J., & Ezell, N. D. B. (2022). *Chem. Eng. Sci.*, 260, 117954

3.0 RK Parameters Generated (new in red):

Fluorides

LiF-BeF₂, LiF-KF, NaF-KF, NaF-LiF, NaF-ThF₄, LiF-UF₄, LiF-ZrF₄, LiF-ThF₄, NaF-ZrF₄, NaF-UF₄, **KF-ZrF₄**, **NaF-BeF₂**

Chlorides

LiCl-KCl, KCl-MgCl₂, KCl-NaCl, KCl-UCl₃, KCl-UCl₄, NaCl-LiCl, **NaCl-UCl₄**, **NaCl-UCl₃**, **LiCl-UCl₃**, **LiCl-UCl₄**, **UCl₃-UCl₄**, **NaCl-ThCl₄**

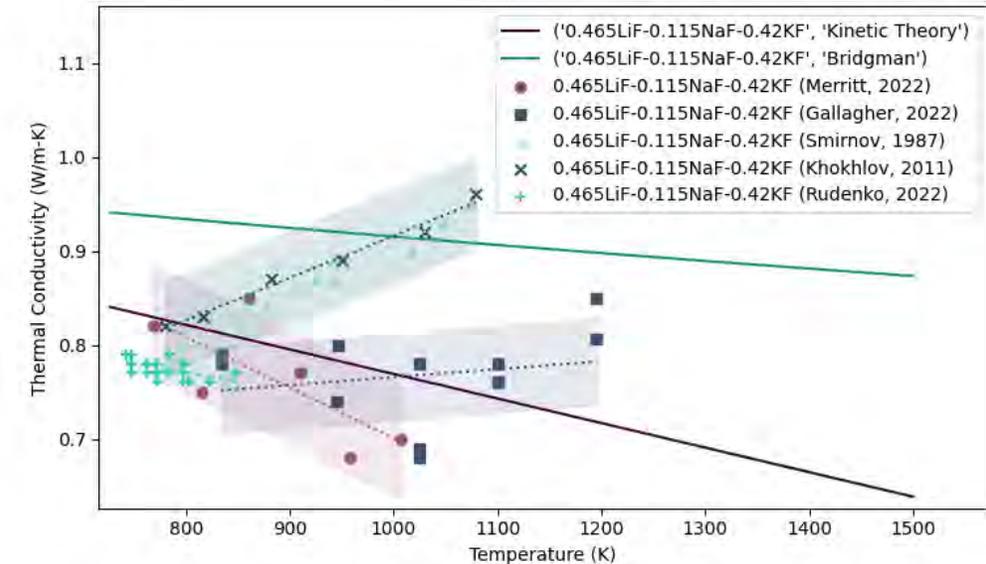
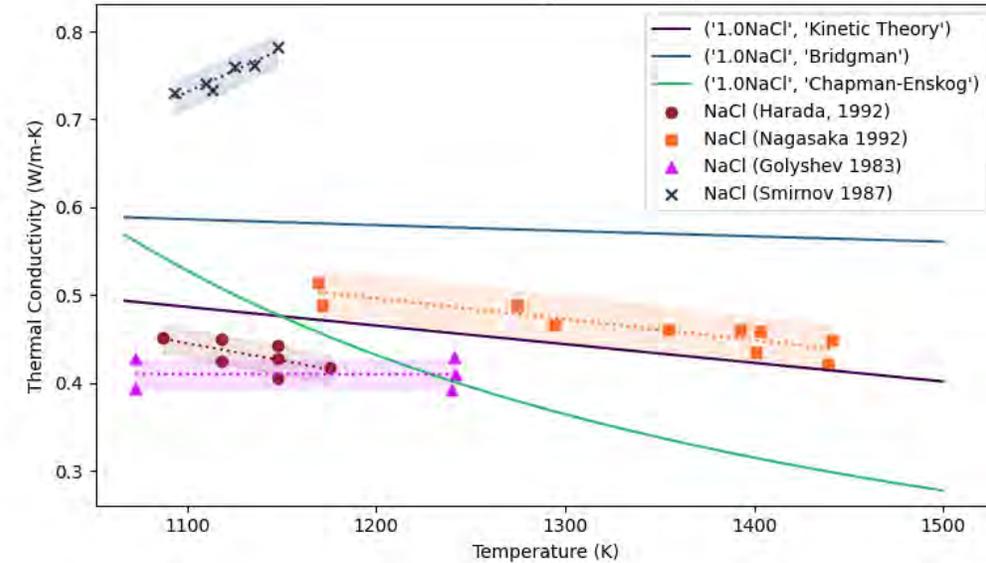
Reciprocal Salts

KCl-KF, **NaCl-NaF**, **NaCl-ZrF₄**, **KCl-ZrF₄**

Preliminary Work: Thermal Conductivity Estimation

- Evaluating thermal conductivity estimation methods with measurement data
- End goal to develop thermal conductivity prediction methods for actinide-bearing salts.
 - Model must capture temperature and composition dependence of phonon mean free path

	Quasi-Lattice Models		Fitting Methods	Dilute Gas Models
	Bridgman-type [1]	Kinetic theory (Gheribi) [2]	Corresponding states, semi-empirical models [3]	Chapman-Enskog [4]
Temperature Dependence	Negative; based on temp-dependent sound velocity	Negative; based on thermal expansivity at melting point scaled with temperature change and composition	Matches temperature-dependent behavior of fitted data	Negative; Based on temp-dependent extrapolation of viscosity
Limitations	Does not consider dissociated interatomic behavior (prevalent in molten salt ions)	Requires fitting to empirical data (KCl) to scale the phonon mean free path relationship	May not be capable of extrapolating to salt and compositional variation.	Does not capture the temperature dependence of salts.



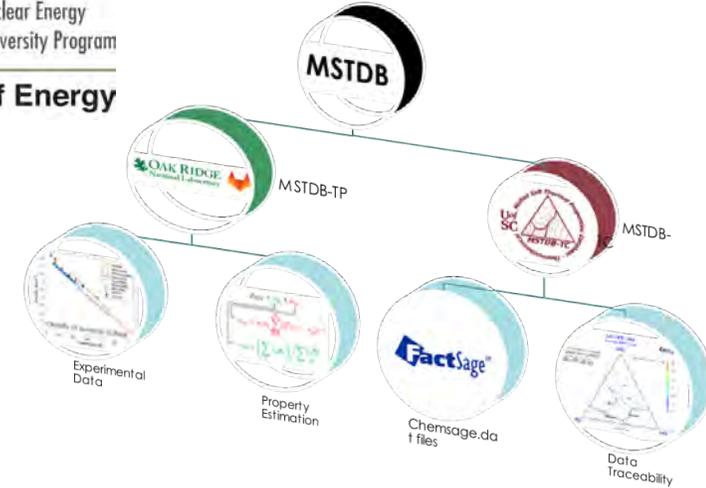
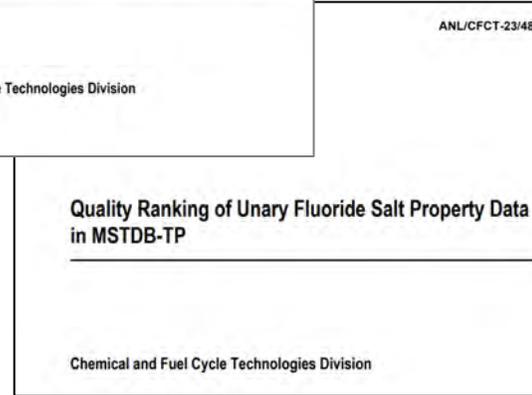
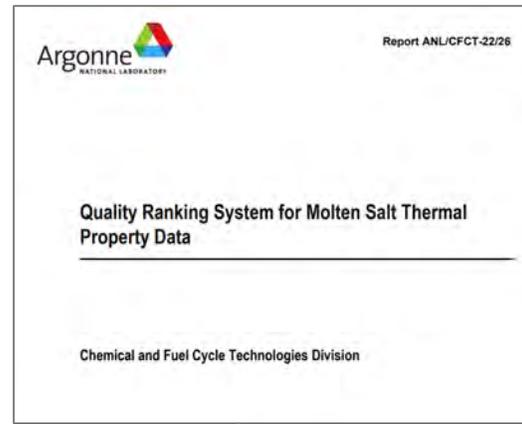
[1] Kincaid, J. F., & Eyring, H. (1938). *J. Chem. Phys.*, 6(10), 620-629.
 [2] Gheribi, A. E., Torres, J. A., & Chartrand, P. (2014). *Sol. Energy Mater.*, 126, 11-25.

[3] Nagasaka, Y., & Nagashima, A. (1993). *Int. J. Thermophys.*, 14, 923-936.

[4] Zhao, A. Z. et al., (2021). *J. Appl. Phys.*, 129(23).

Collaborative Efforts

- Working with ANL to apply quality rankings to data in the database (POC: Melissa Rose)
- Worked with universities on NEUP proposals
- Working closely with UoSC to ensure consistency between TP and TC
- Collaborating with AIMD modelers to incorporate simulated data into MSTDB-TP
- Supporting ANL and UMass Lowell in using MSTDB-TP to train NNs for predictive modelling (POCs: Shayan Shahbazi, Stephen Lam)



[1] Nguyen, M. T., Glezakou, V. A., Lonergan, J., McNamara, B., Paviet, P. D., & Rousseau, R. (2021). *J. Mol. Liq.*, 326, 115262.
 [2] Barra Otondo, J. et al. (2023). *Trans. Am. Nuc. Soc.*, 129(1), 482-483.

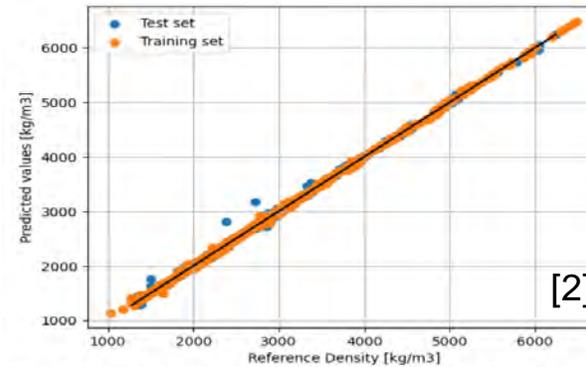
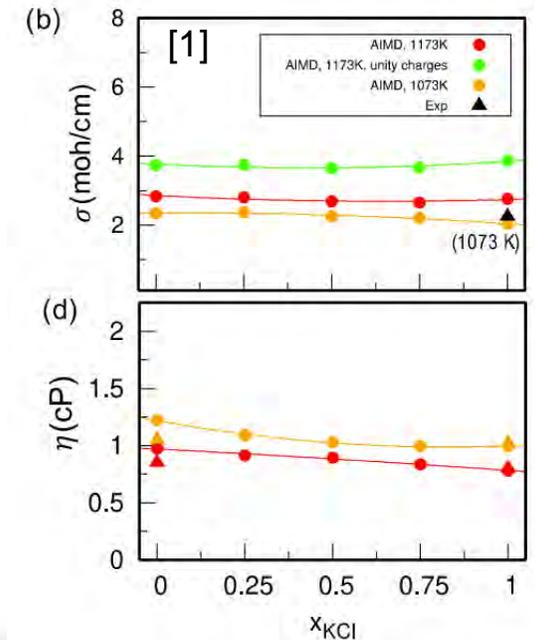


Fig. 2 Experimental vs. DNN predicted bulk density across temperature and composition for Pseudo-unary, binary, ternary and quaternary systems in MSTDB.



MSTDB Website

- New website to capture both MSTDB-TP and TC
 - Contains info about both arms
- Access links and instructions
- Recent News
- List of Publications and Workshop documents
- Contacts

The screenshot shows the top navigation bar of the Oak Ridge National Laboratory website, with links for Home, About, Thermophysical (TP), Thermochemical (TC), Publications, News, and Team. The main heading reads "Molten Salt Thermal Properties Database -- MSTDB". Below this, a paragraph describes the databases: "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."

The screenshot displays the "Publications" section, titled "MSTDB Reference Documents/Publications". It lists several articles with expandable arrows:

- THERMODYNAMIC MEASUREMENTS AND ASSESSMENTS FOR THE LiCl-NaCl-KCl-UCl₃ SYSTEMS
- THERMODYNAMIC ASSESSMENTS OR REASSESSMENTS OF 30 PSEUDO-BINARY AND -TERNARY SALT SYSTEMS
- APPLICATION OF THE REDLICH-KISTER EXPANSION FOR ESTIMATING THE DENSITY OF MOLTEN FLUORIDE PSEUDO-TERNARY SALT SYSTEMS OF NUCLEAR INDUSTRY INTEREST
- DEVELOPMENT AND APPLICATION OF A THERMOCHEMICAL DATABASE (MSTDB-TC) FOR MODELING CORROSION IN MOLTEN SALT REACTORS
- THERMODYNAMIC ASSESSMENT OF LITHIUM HALIDE RECIPROCAL SALT SYSTEMS FOR ENERGY APPLICATIONS
- MODELING METALLIC HALIDE LOCAL STRUCTURES IN SALT MELTS USING A GENETIC ALGORITHM
- DEVELOPMENT OF THE MOLTEN SALT THERMAL PROPERTIES DATABASE - THERMOCHEMICAL (MSTDB-TC), EXAMPLE APPLICATIONS, AND LiCl-RbCl AND UF₃-UF₄ SYSTEM ASSESSMENTS
- EMPIRICAL ESTIMATION OF DENSITIES IN NaCl-KCl-UCl₃ AND NaCl-KCl-YCl₃ MOLTEN SALTS USING REDLICH-KISTER EXPANSION
- CORRELATIONAL APPROACH TO PREDICT THE ENTHALPY OF MIXING FOR CHLORIDE MELT SYSTEMS

The screenshot shows a navigation menu with the following categories and sub-items:

- Pseudo-binary Systems
 - FLUORIDES
 - CHLORIDES
 - IODIDES
 - RECIPROCAL SALTS
- Pseudo-ternary Systems
 - FLUORIDES
 - CHLORIDES
 - IODIDES
 - RECIPROCAL SALTS
 - TERNARY RECIPROCAL SALT SYSTEMS
- Higher-Order Systems
 - FLUORIDES
 - CHLORIDES
 - RECIPROCAL TETRAHEDRA
 - QUATERNARY AND HIGHER ORDER RECIPROCAL SALT SYSTEMS

The screenshot displays the "NEW RELEASE" section, titled "Molten Salt Thermal Properties Database-Thermochemical (MSTDB-TC) Ver. 3.0". It includes a sub-section for "Molten Salt Thermal Properties Working Group Hosts MSTDB Workshop" and a link to "Previous MSTDB workshop content publicly available".

NEW RELEASE: Molten Salt Thermal Properties Database-Thermochemical (MSTDB-TC) Ver. 3.0

The Molten Salt Thermal Properties Database-Thermochemical (MSTDB-TC) Ver. 3.0 (succeeding Ver. 2.0) is now available for general use. Access procedures remain the same as for earlier versions.

Molten Salt Thermal Properties Working Group Hosts MSTDB Workshop

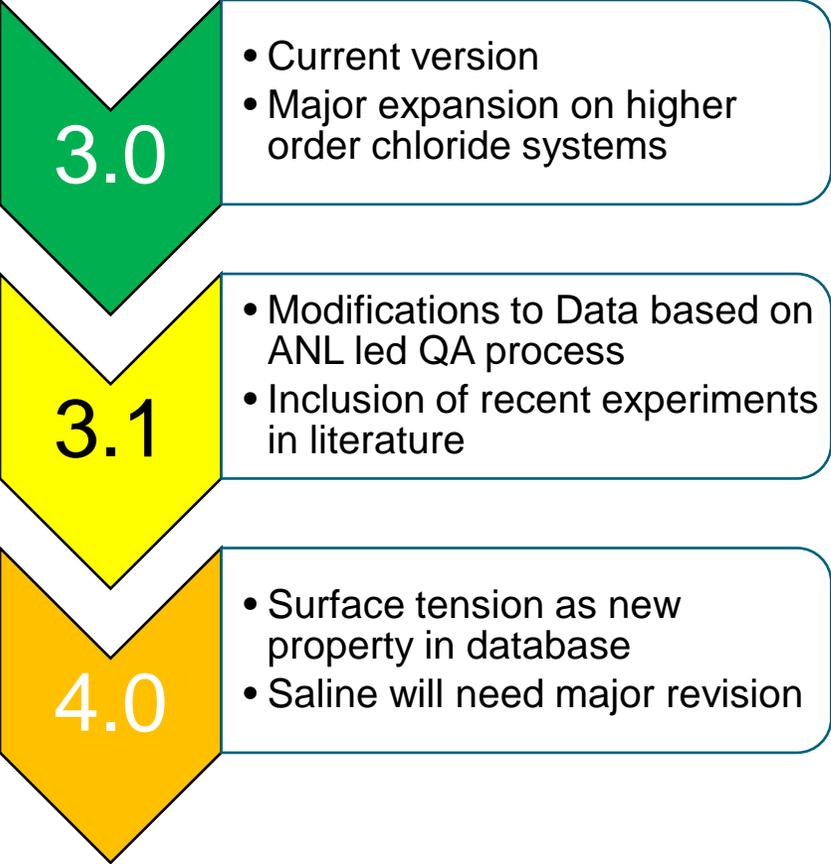
The Molten Salt Thermal Properties Working Group hosted a virtual workshop on the MSTDB virtually on April 25, 2023.

Previous MSTDB workshop content publicly available

Example phase diagram of KCl-CrCl₂ from MSTDB-TC, presented by Dr. Ted Basermann in the 2021 Virtual Workshop for the Molten Salt Thermal Properties Working Group.

MSTDB-TP Update Plan

Database Updates

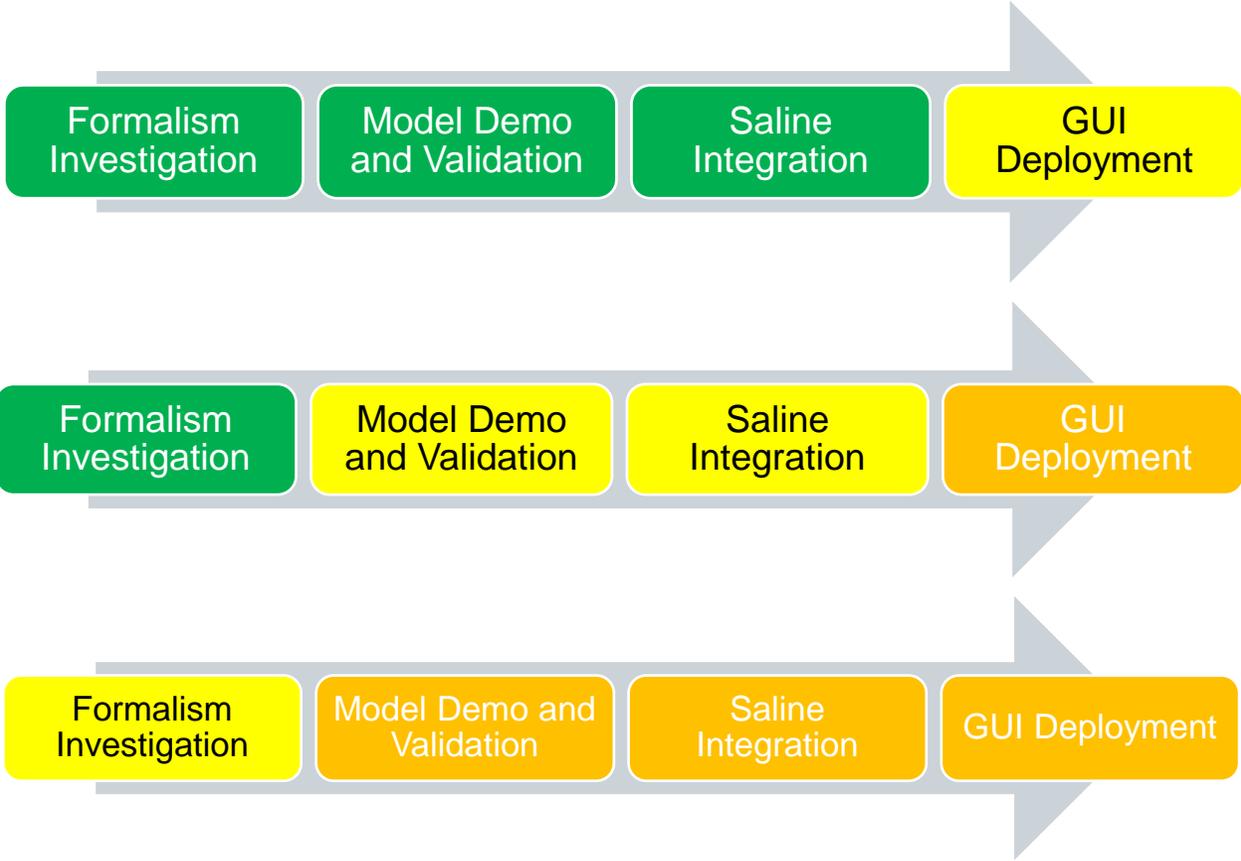


Density RK Model Capability

Viscosity RK Model Capability

Thermal Conductivity Model Capability

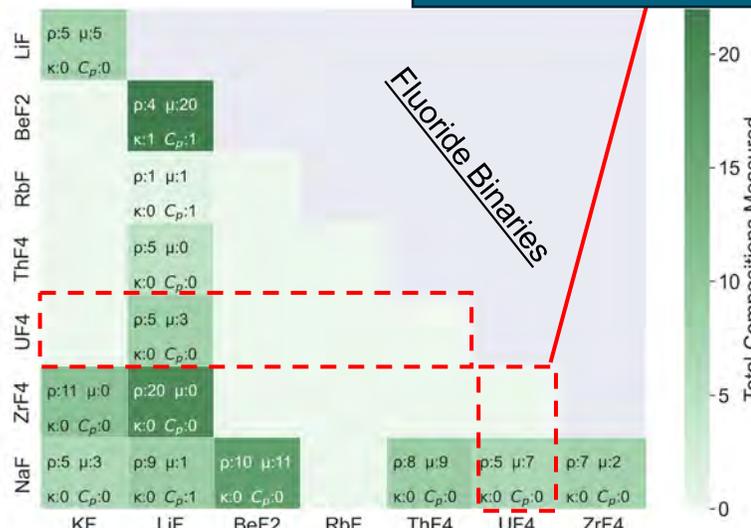
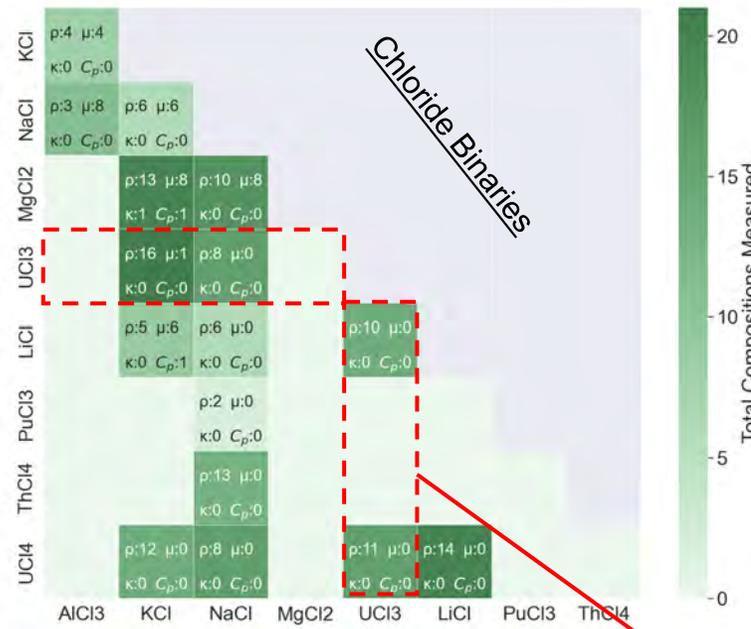
Predictive Model Updates



Legend: ■ = Completed, ■ = In progress, ■ = Future

Requests to experimentalists/Modelers: Let's fill critical gaps!

- Given the interest in UF4 and UCl3 bearing mixtures by developers, target gaps in associated pseudo-binaries
 - Allows for more RK parameters to be generated
- More ternary data would also be useful
 - RK model validation
- Thermal conductivity and heat capacity of mixtures is still sparse
- AIMD may be great to target really challenging gaps
 - For example, pure PuCl3 density has been generated in: Duemmler, K., Andersson, D., & Beeler, B. (2024). J. Nucl. Mat., 591, 154902.



Ternaries

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	5	0	0
KF-LiF-NaF	1	1	1	1
BeF2-LiF-UF4	36	36	0	0
LiF-ThF4-UF4	1	0	0	0
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	0
KF-MgCl2-NaF	1	0	0	0
KF-NaF-UF4	2	1	0	1
KF-NaF-ZrF4	1	1	0	0
LiF-NaF-ZrF4	9	0	0	0
NaF-UF4-ZrF4	5	3	0	3
RbF-UF4-ZrF4	2	2	0	1

Sparse heat capacity and thermal conductivity

Thank you

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

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NUCLEAR ENERGY