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NEAMS Nuclear Energy Advanced Modeling and Simulation

Molten Salt Reactor PROGRAM

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

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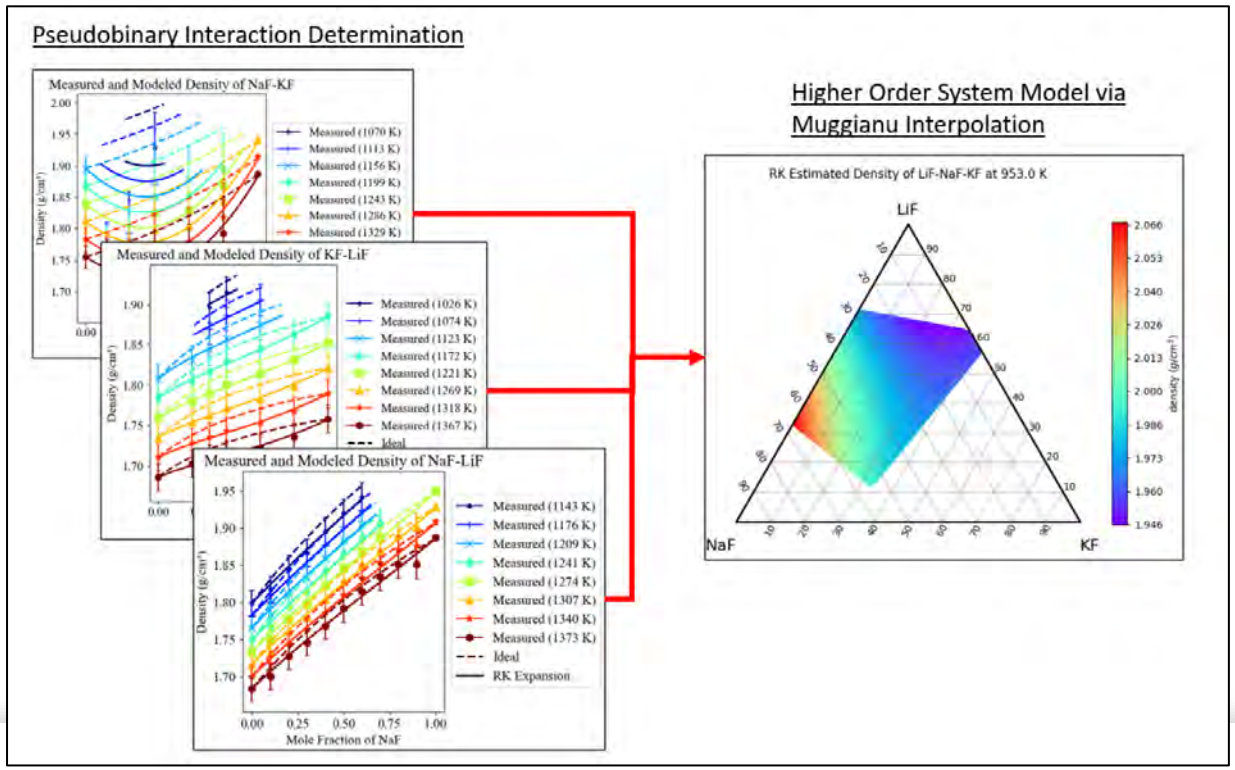
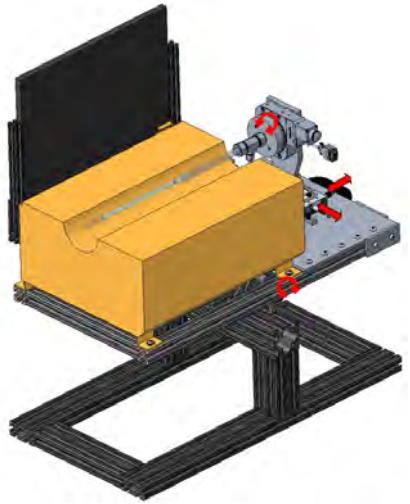
OAK RIDGE National Laboratory

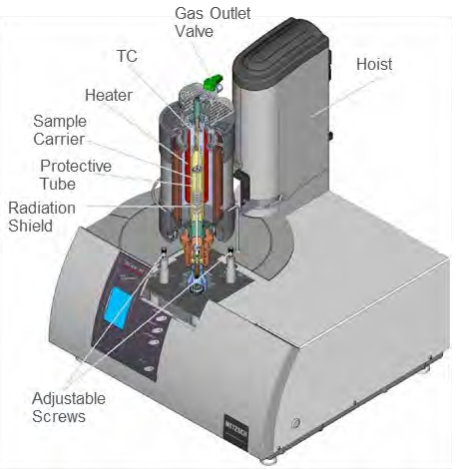
Annual MSR Campaign Review Meeting 16-18 April 2024

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

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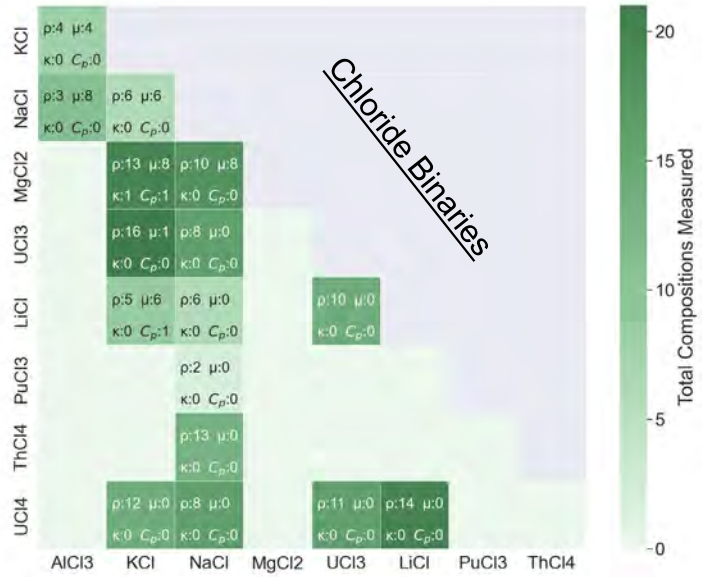
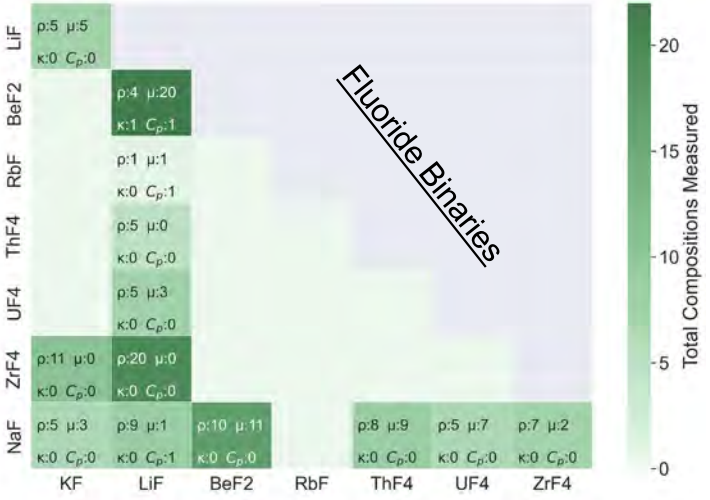
UNIVERSITY OF South Carolina | Molten Salt Reactor PROGRAM

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	1	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	1	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	0	0	1
UCl4	1	0	0	0
UF3	0	0	0	1
UF4	1	1	0	1
ZrCl4	1	1	0	0
ZrF4	1	0	0	0





Ternaries

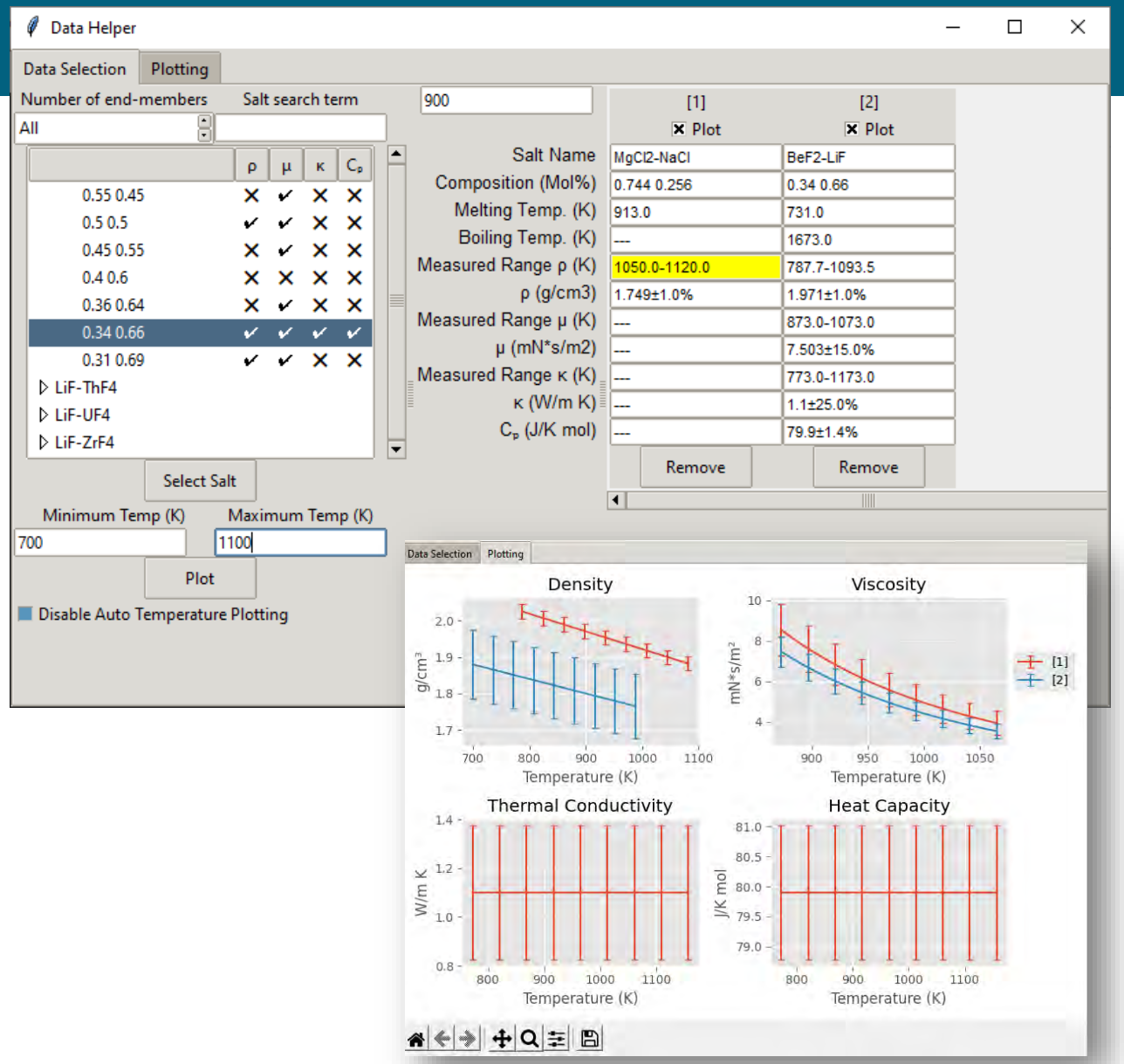
Salt	Measurements			
	ρ	μ	κ	c_p
KCl-LiCl-NaCl	4	0	0	0
KCl-LiCl-UCl3	18	0	0	0
KCl-LiCl-UCl4	18	0	0	0
KCl-NaCl-UCl3	18	0	0	0
KCl-UCl3-UCl4	32	0	0	0
AlCl3-LiCl-NaCl	10	10	0	0
LiCl-UCl3-UCl4	21	0	0	0
BeF2-LiF-ThF4	3	2	0	0
BeF2-LiF-ZrF4	1	0	0	0
BeF2-LiF-NaF	5	5	0	0
KF-LiF-NaF	1	1	1	1
BeF2-LiF-UF4	36	36	0	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

Quaternaries

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

MSTDB-TP Tools

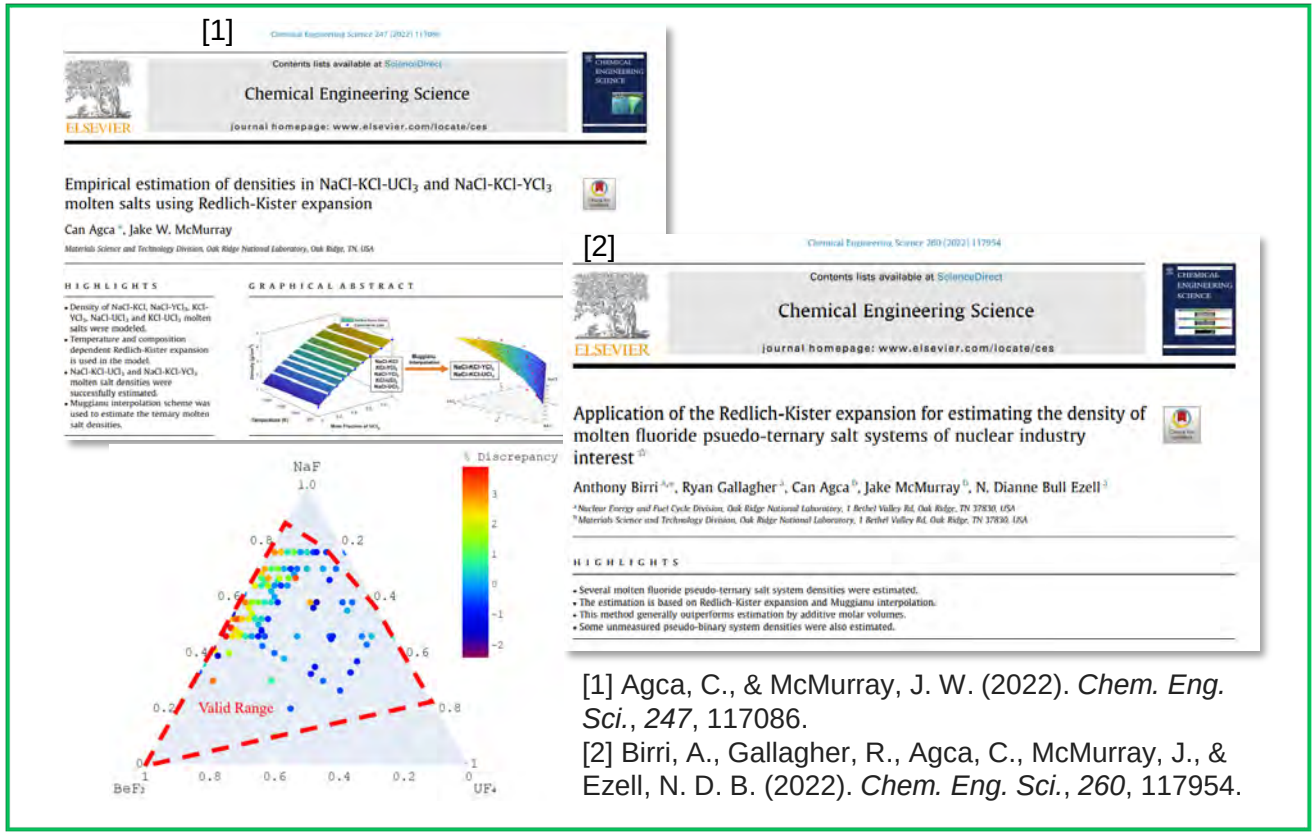
- MSTDB-TP is a large, difficult to navigate .csv file
- Saline is the MSTDB-TP API
  - Provides a stable C++ interface for obtaining supported properties (density, viscosity, heat capacity, and thermal conductivity)
  - Designed for integration with other NEAMS codes
- The MSTDB-TP GUI allows for easier navigation and visualization of the data
  - Can provide access to beta version, official GitLab deployment coming soon
- GUI Contact: Nick Termini terminc@ornl.gov
- Saline Contact: Shane Henderson hendersonsc@ornl.gov



Redlich-Kister Modeling Efforts

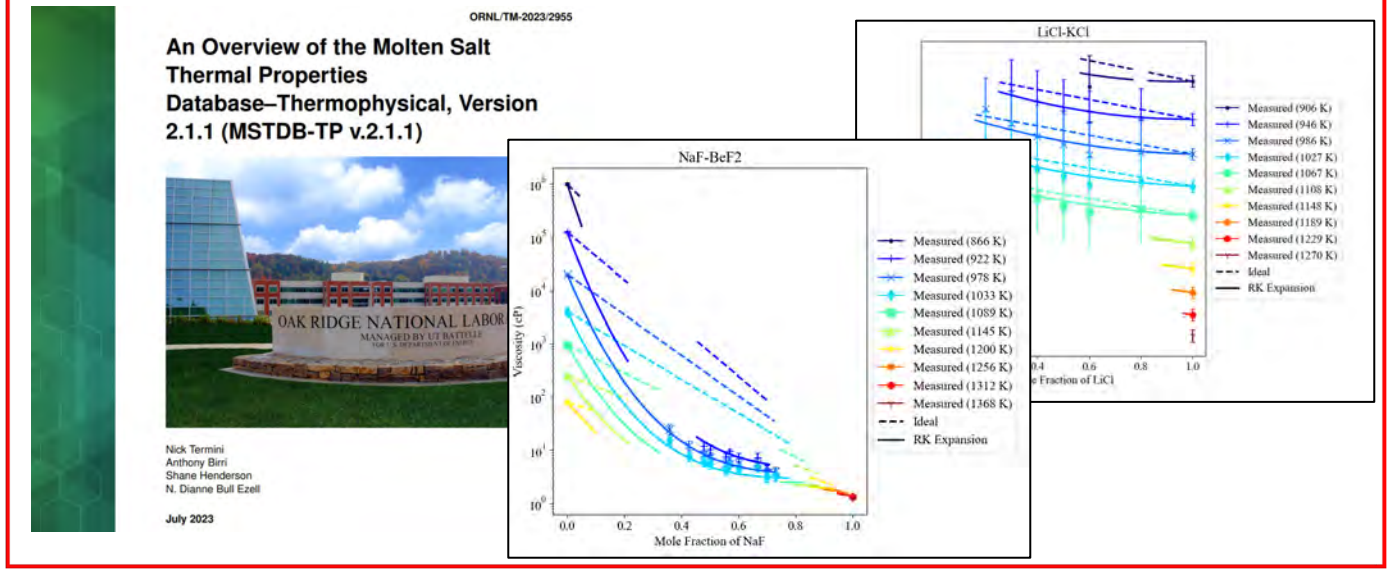
- Semi-empirical solution model which can be used to predict thermophysical properties
  - Fed data from MSTDB-TP
  - Used to interpolate/extrapolate over compositional/temperature domain of the salt matrix
- Motivation: We can only make measurements across the national laboratories so fast
  - Limited 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] 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



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

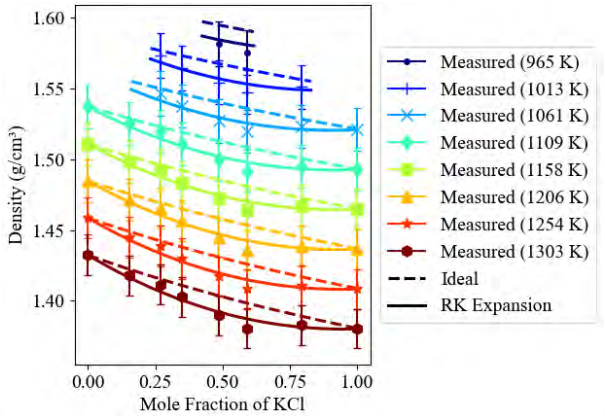
Pseudo-binary RK example: KCl-NaCl

Density

$$\rho_{mix} = \rho_{id} + \rho_{ex}$$

$$\rho_{id} = \left(\sum_i x_i M_i\right) / \sum_i \frac{x_i M_i}{\rho_i}$$

$$\rho_{ex} = x_1 x_2 \sum_{j=1}^{n} L_j^{12} (x_1 - x_2)^{j-1}$$

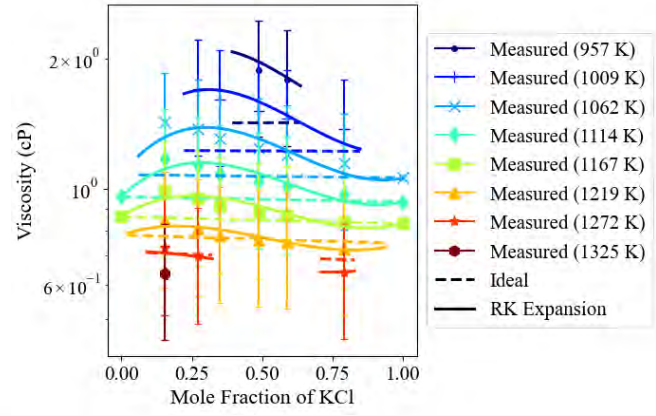


Viscosity

$$\ln(\eta_{mix}) = \ln(\eta_{id}) + \ln(\eta_{ex})$$

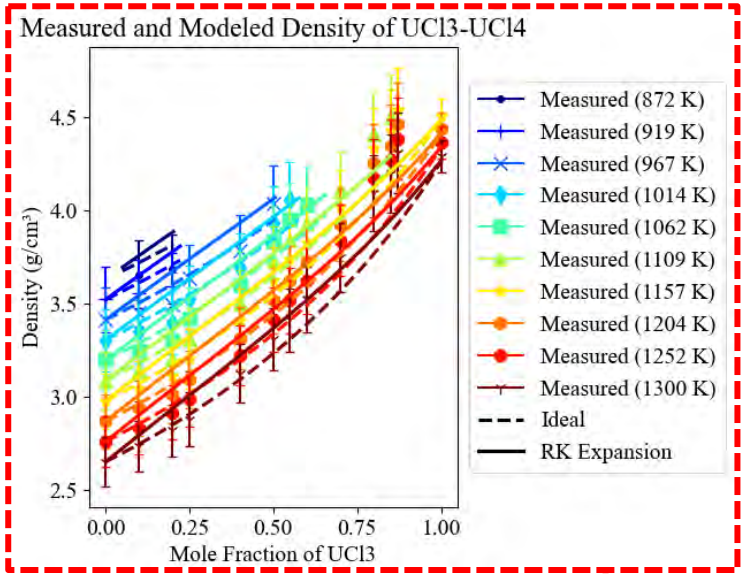
$$\ln(\eta_{id}) = \sum_i x_i \ln(\eta_i)$$

$$\ln(\eta_{ex}) = x_1 x_2 \sum_{j=1}^{n} L_j^{12} (x_1 - x_2)^{j-1}$$



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):

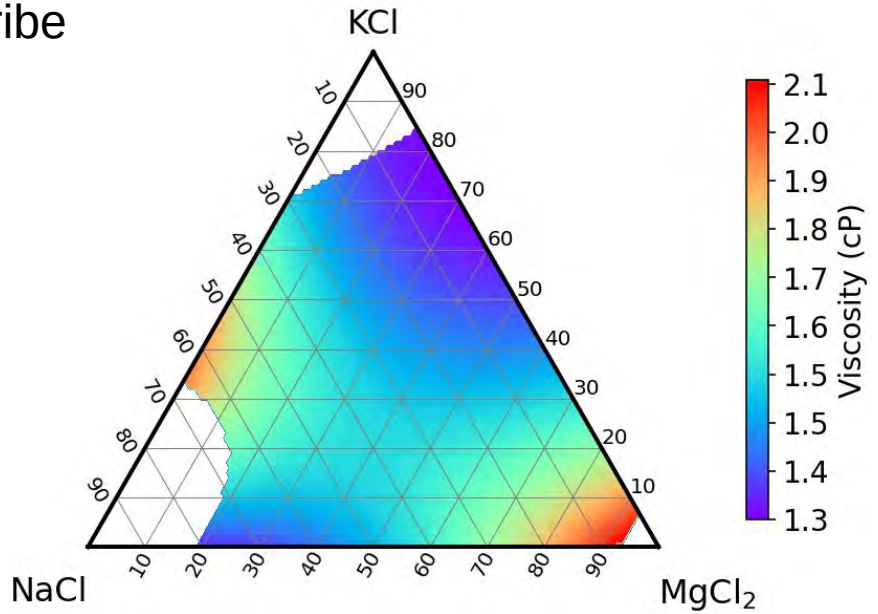
Fluorides
LiF-BeF2, LiF-KF, NaF-KF, NaF-LiF, NaF-ThF4, LiF-UF4, LiF-ZrF4, LiF-ThF4, NaF-ZrF4, NaF-UF4, KF-ZrF4, NaF-BeF2

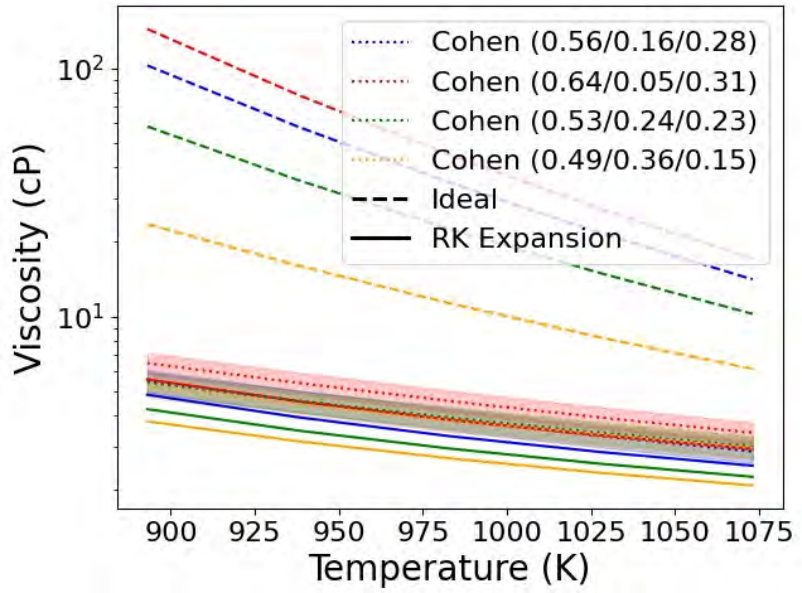
Chlorides
LiCl-KCl, KCl-MgCl2, KCl-NaCl, KCl-UCl3, KCl-UCl4, NaCl-LiCl, NaCl-UCl4, NaCl-UCl3, LiCl-UCl3, LiCl-UCl4, UCl3-UCl4, NaCl-ThCl4

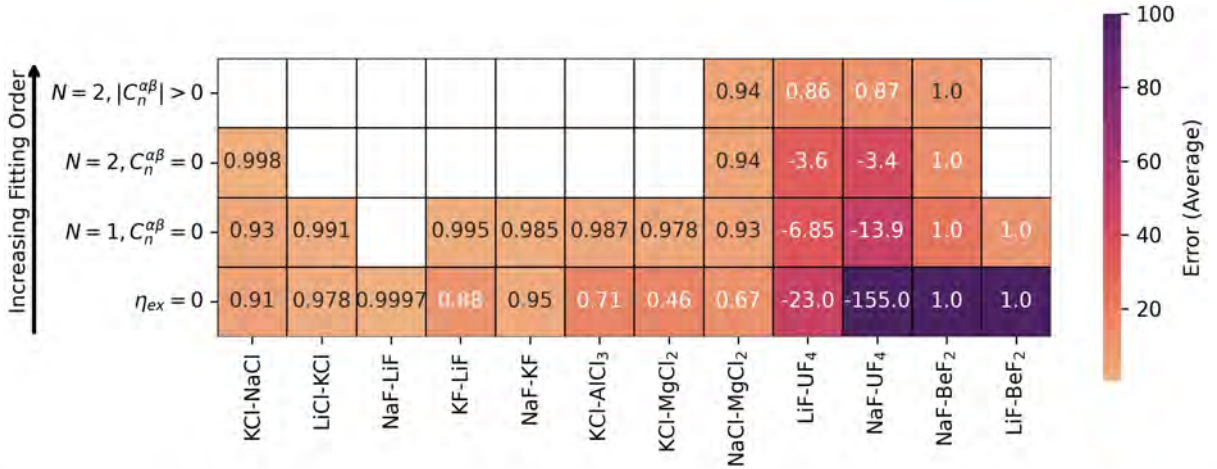
Reciprocal Salts
KCl-KF, NaCl-NaF, NaCl-ZrF4, KCl-ZrF4

Current Status of Redlich-Kister Viscosity Modeling

- Demonstrated an RK formalism which is flexible and generalizable to describe mixture viscosity based on binary interactions
  - Flexible scheme to prevent overfitting
- Good predictive capabilities for higher order systems
  - Non-ideality handled reasonably well, just based on binary interactions
  - Some error is expected due to structure/complexation differences
- **Manuscript on this submitted to Chemical Engineering Science**
- Current work to integrate into Saline



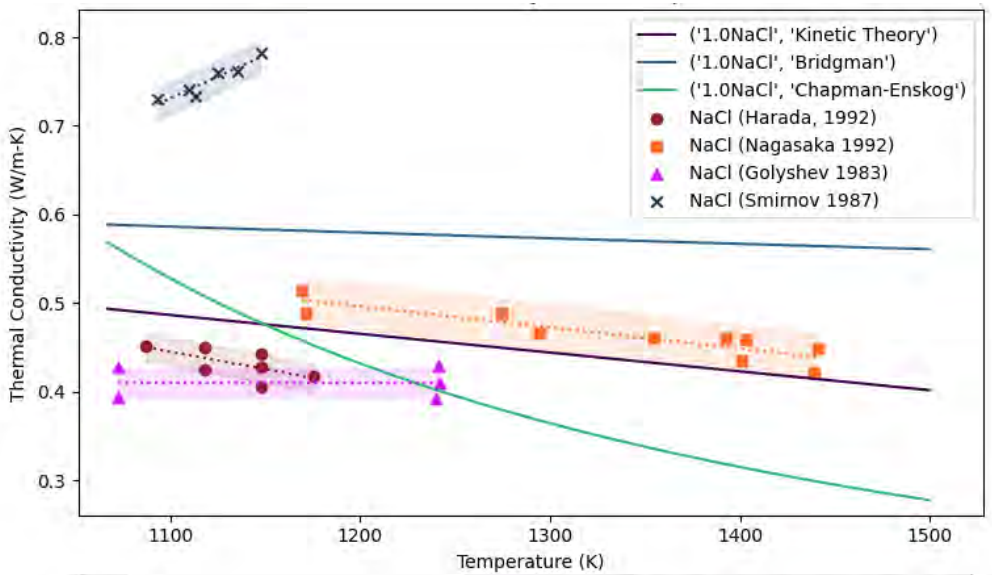


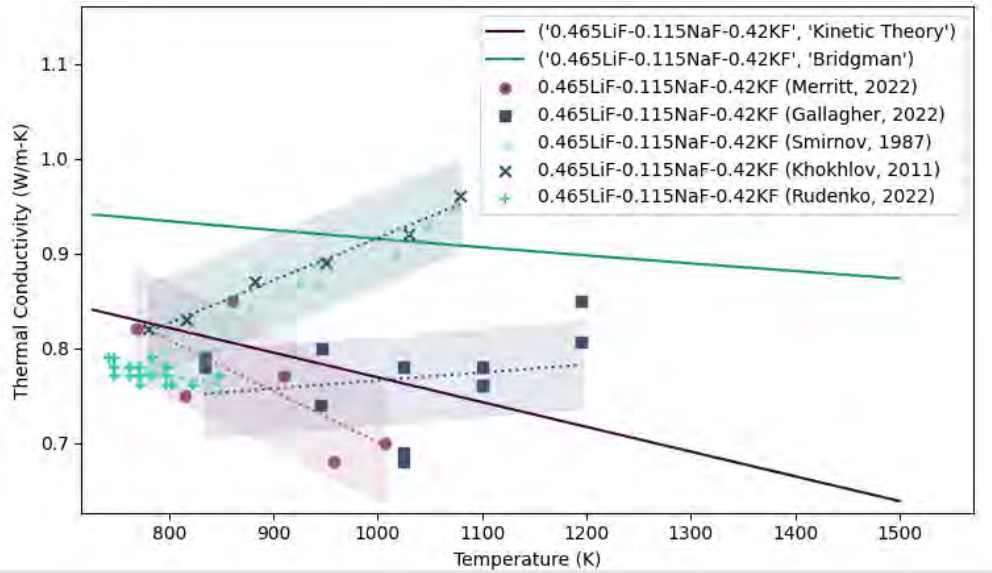


Preliminary Work: Thermal Conductivity Estimation

- 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.



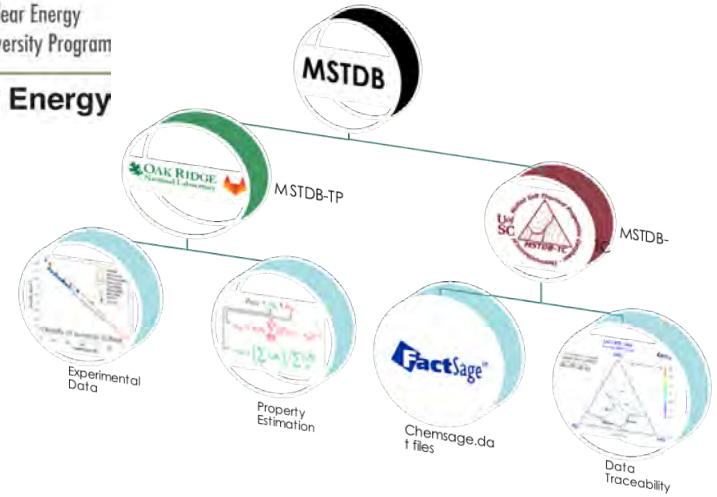


[1] Kincaid, J. F., & Eyring, H. (1938). *J. Chem. Phys.*, *6*(10), 620-629.
[2] Gheribi, A. E., Torres, J. A., & Chartrand, P. (2014). *Sol. Energy Mater.*, *126*, 11-25.
[3] Nagasaka, Y., & Nagashima, A. (1993). *Int. J. Thermophys.*, *14*, 923-936.
[4] Zhao, A. Z. et al., (2021). *J. Appl. Phys.*, *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)

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



[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.

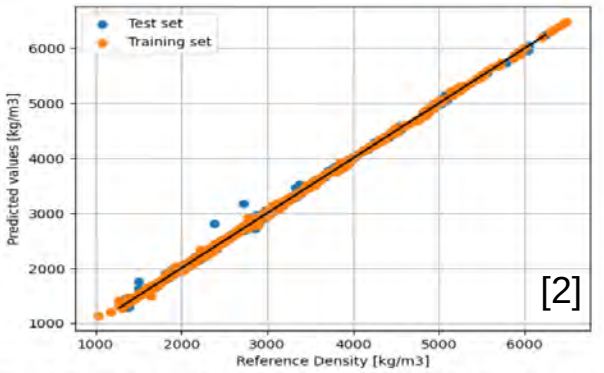
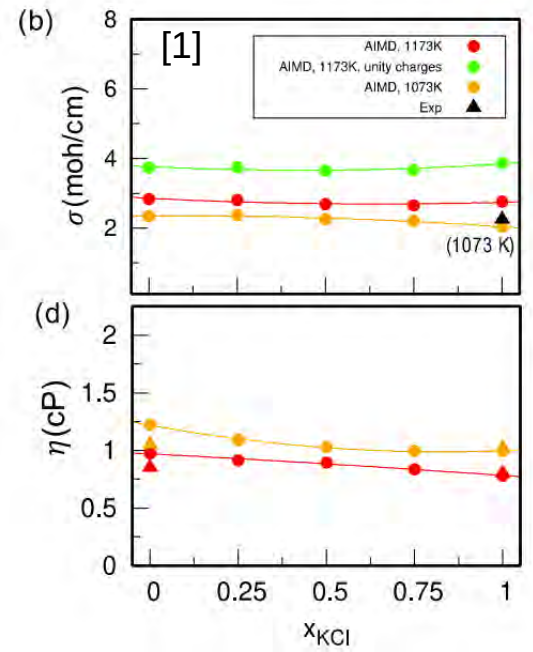


Fig. 2 Experimental vs. DNN predicted bulk density across temperature and composition for Pseudo-unary, binary, ternary and quaternary systems in MSTDB.



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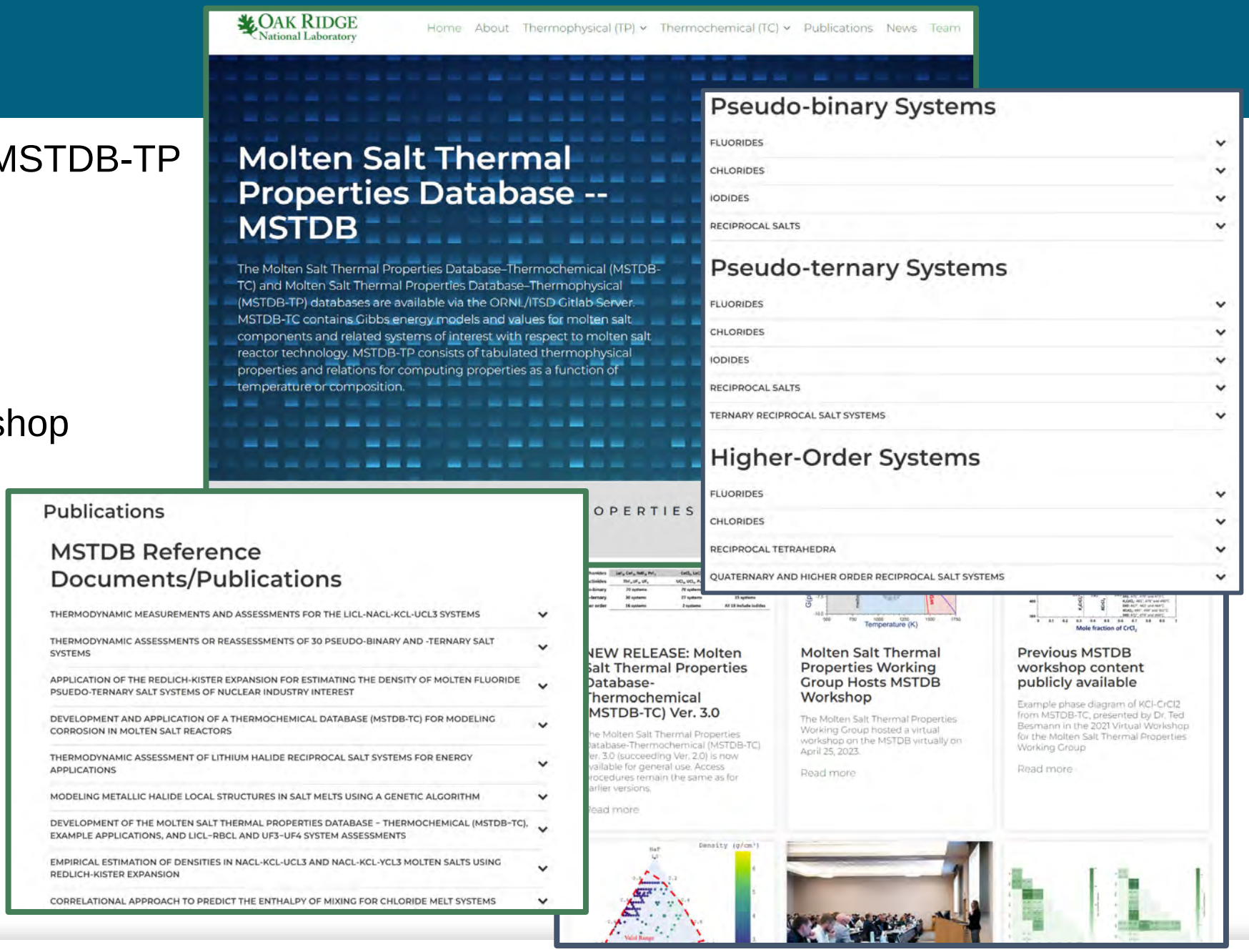
MSTDB Website

- 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



MSTDB-TP Update Plan

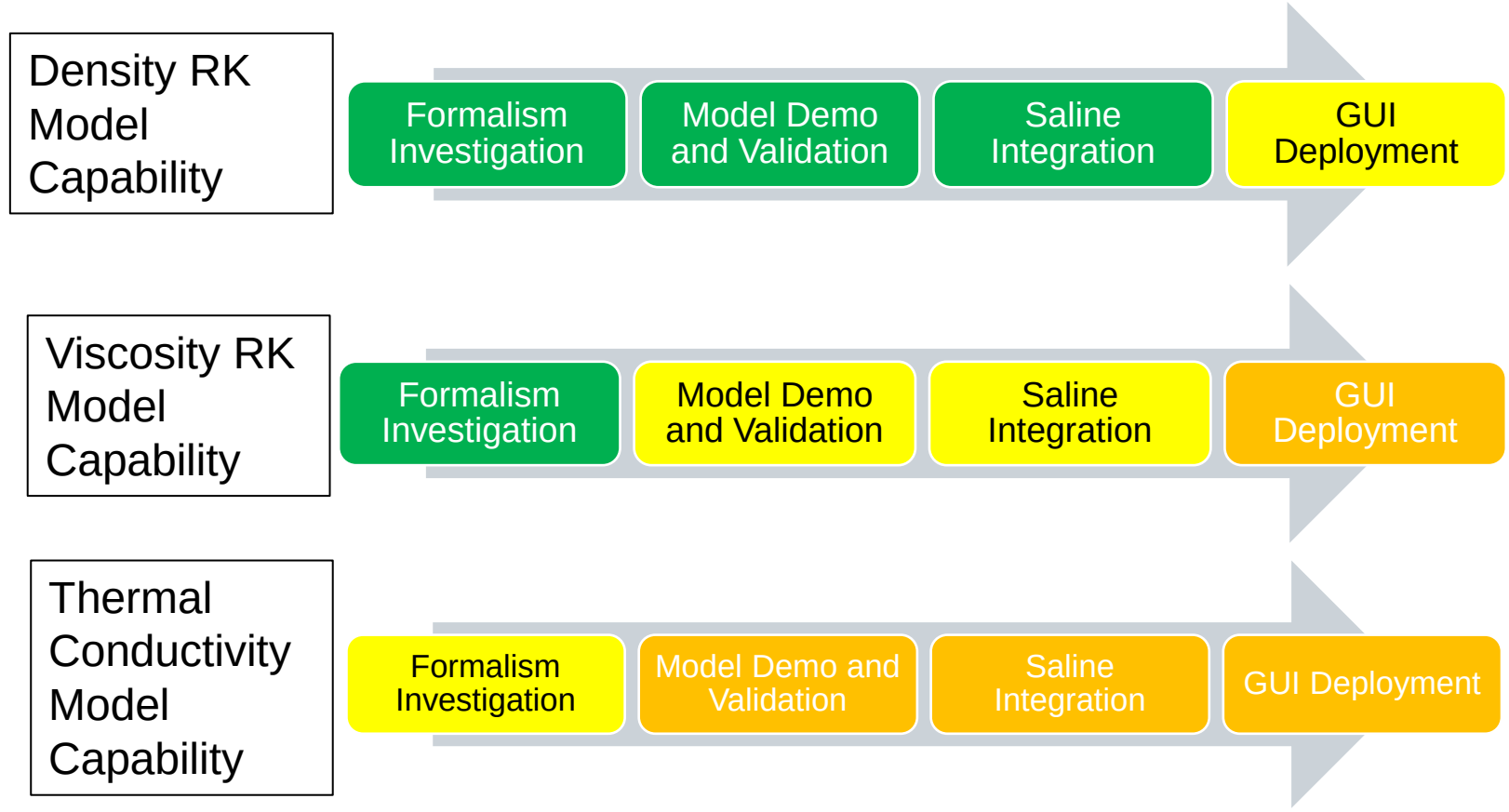
Database Updates

3.0
- Current version
- Major expansion on higher order chloride systems

3.1
- Modifications to Data based on ANL led QA process
- Inclusion of recent experiments in literature

4.0
- Surface tension as new property in database
- Saline will need major revision

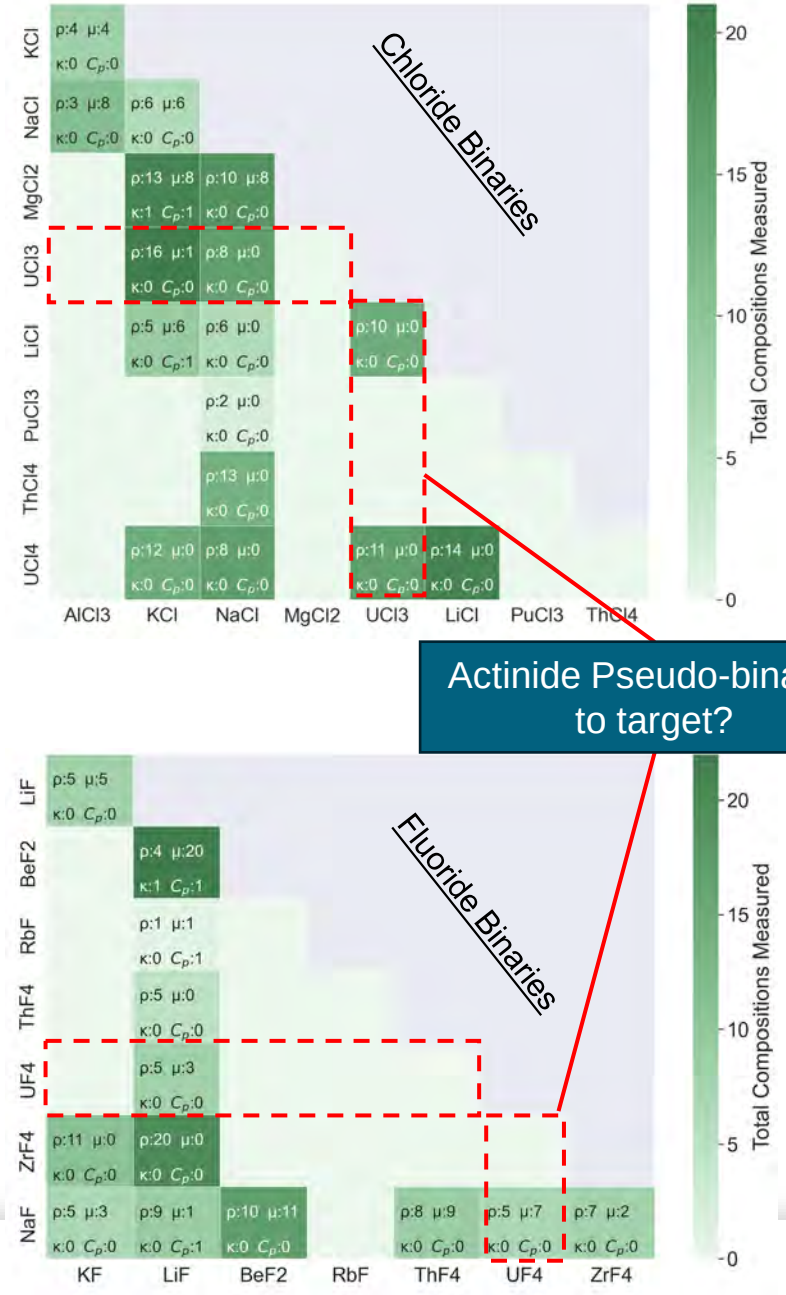
Predictive Model Updates



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.



Actinide Pseudo-binaries to target?

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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