# Thermophysical modeling of molten salts

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# Vision/Mission

- The Molten Salt Thermal Properties Database (MSTDB) is a database of models and model parameters that will represent salt solution thermal property behavior as a function of temperature and composition
  - **T**hermo**c**hemical division is designated MSTDB-TC
  - **T**hermophysical **p**roperties division is designated MSTDB-TP

# Molten Salt Thermophysical Database 1.0

- **MSTDB-TP Version 1.0 finalized (open access soon to be available)**

- Type of data (along with references and uncertainty)
  - Melting temperature
  - Boiling temperature
  - Density
  - Viscosity
  - Thermal Conductivity
  - Heat capacity

- 62 entries currently: 27 pure, 8 binaries, 10 ternaries & 5 quaternaries

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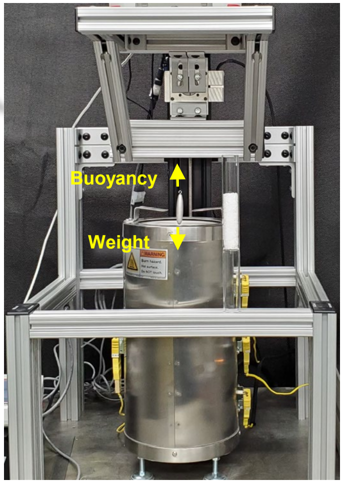
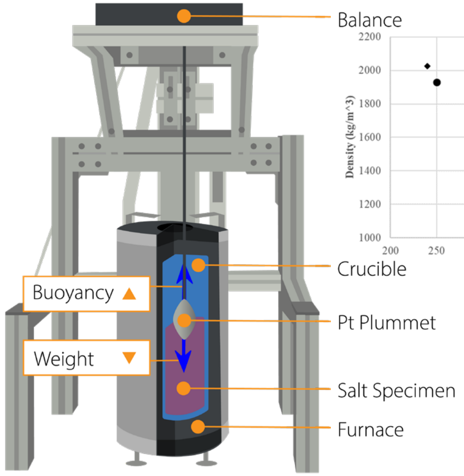
- 62 entries currently: 27 pure, 8 binaries, 10 ternaries & 5 quaternaries
  - Thermal conductivity needs data through either experiments or theoretical studies

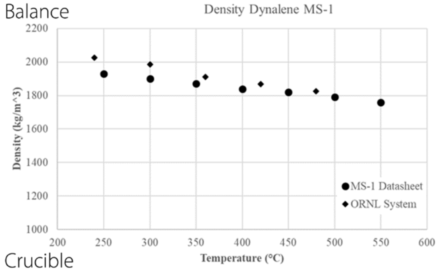
# Thermophysical Characterizations

## Density

**Archimedes Bob Density Measurement Apparatus**

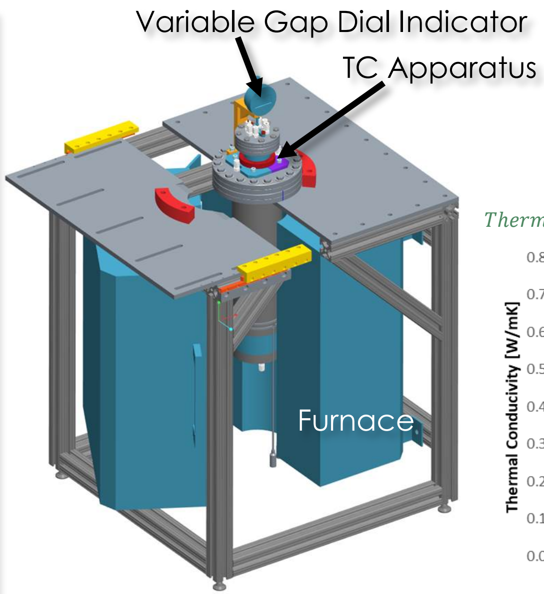


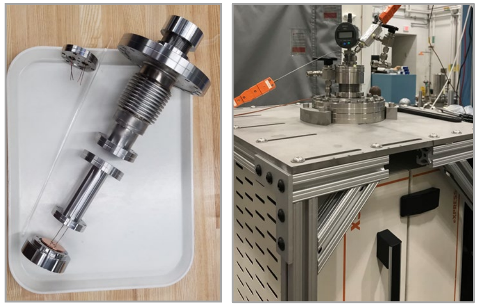




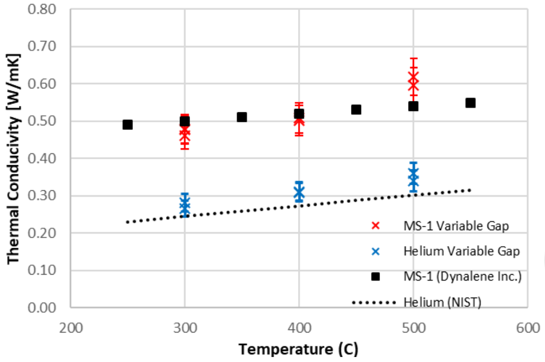
**Alternate methods:**
Optical dilatometry
X-ray dilatometry

## Thermal Conductivity

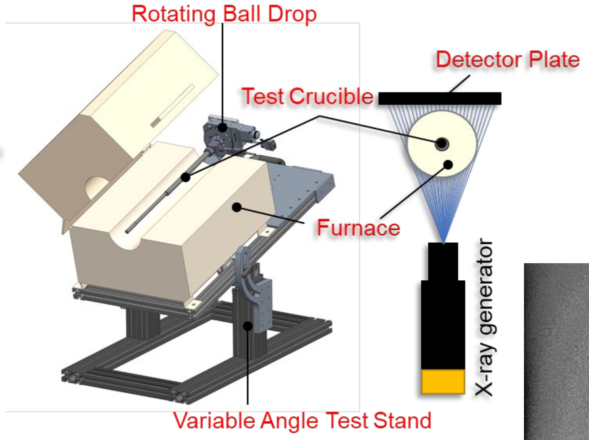


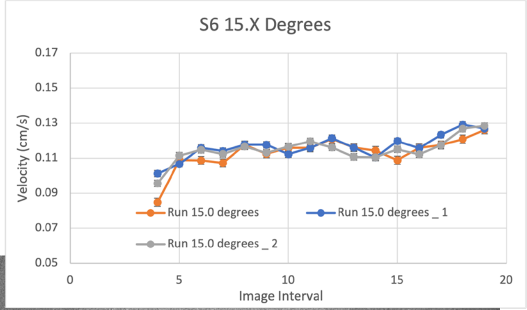


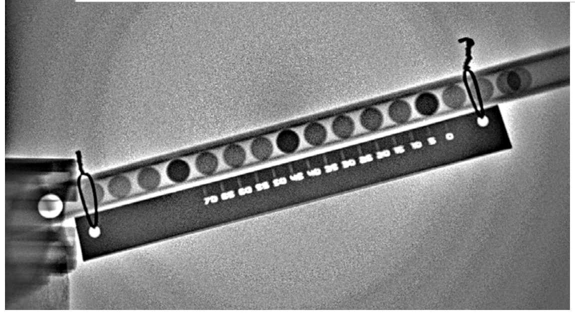
$$\text{Thermal Resistance} = \frac{\text{Change in temperature across gap}}{\text{heat flux}}$$



## Viscosity

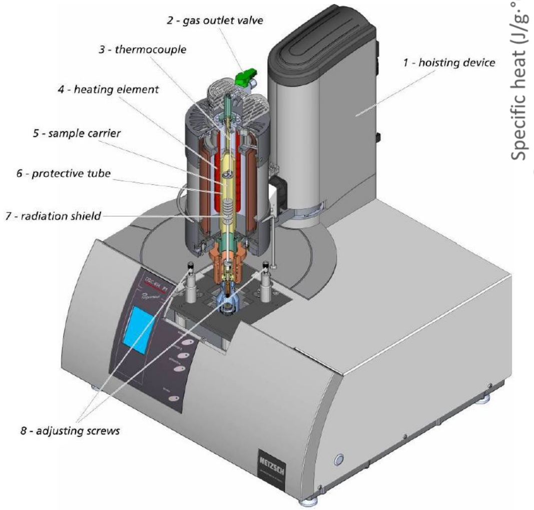


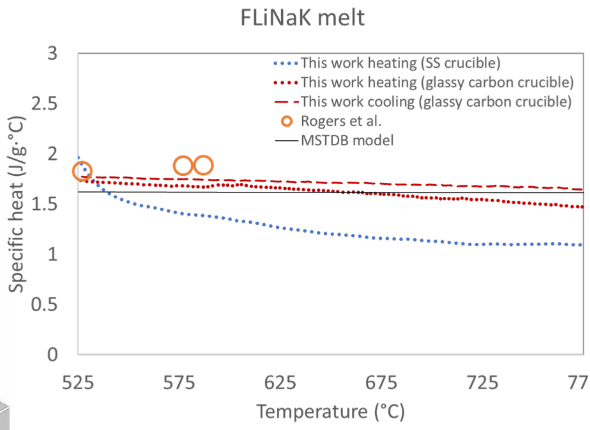




**Equivalent to falling-ball optical measurements**

## Specific Heat





# Pure salts of interest in MSR campaign

## The pure salts of interest with their melting temperatures for thermophysical properties

| Salt | Melting T (°C) | Salt | Melting T (°C) |
|---|---|---|---|
| $CeCl_3$ | 822 | $CeF_3$ | 1432 |
| CsCl | 645 | $CrF_3$ | 1404 |
| LiCl | 610 | CsF | 703 |
| $MgCl_2$ | 714 | KF | 858 |
| $NdCl_3$ | 758 | LiF | 848 |
| $PuCl_3$ | 767 | NaF | 995 |
| $SrCl_2$ | 873 | $NdF_3$ | 1377 |
| $ThCl_4$ | 770 | $PuF_3$ | 1426 |
| $UCl_3$ | 841 | $SrF_2$ | 1473 |
| $UCl_4$ | 590 | $ThF_4$ | 1110 |
| $ZrCl_4$ | 437 | $UF_3$ | 1495 |
| **CsI** | 634 | $ZrF_4$ | 910 |
| | | $BeF_2$ | 548 |

Orange: Immediate goal

Yellow: Near term goal

White: Long term goal


ORNL/SPR-2020/1865

Roadmap for thermal property measurements of Molten Salt Reactor systems

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D. Andersson
N Ezell

March 2021

Oak Ridge National Laboratory

Mcmurray, Jake W., et al. Roadmap for thermal property measurements of Molten Salt Reactor systems. No. ORNL/SPR-2020/1865. Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States), 2021.

# Binary salt characterizations

- Binary molten salt systems help with modeling of higher order systems
- Molten salts of from tables are impactful for reactor developers
- Experimental or molecular dynamics studies needed

**Key**
**A**: Density
**B**: Viscosity
**C**: Thermal conductivity
**D:** Heat capacity

Chloride

| | BeF2 | KF | LiF | NaF | ThF4 | UF3 | UF4 |
|---|---|---|---|---|---|---|---|
| **KF** | B | | | | | | |
| **LiF** | A, B, D | A, B, C, D | | | | | |
| **NaF** | A, B | A, B, C | A, B, C, D | | | | |
| **ThF4** | | A, B | A, B, D | A, B | | | |
| **UF3** | | | | | | | |
| **UF4** | | A, B | A, B | A, B | | | |
| **ZrF4** | | | A | A, B, D | | | |

Fluoride

| | AlCl3 | KCl | LiCl | MgCl2 | NaCl | PuCl3 | ThCl4 | UCl3 | UCl4 |
|---|---|---|---|---|---|---|---|---|---|
| **KCl** | A, B | | | | | | | | |
| **LiCl** | A | A, B, D | | | | | | | |
| **MgCl2** | | A, B, D | A, B | | | | | | |
| **NaCl** | A, B | A, B, D | A, D | A, B | | | | | |
| **PuCl3** | | | | | | | | | |
| **ThCl4** | | A | | | A | | | | |
| **UCl3** | | A, B | A | | A, B | | | | |
| **UCl4** | | A, B | A | A | A, B | | | | |
| **ZrCl4** | | A | | | | | | | |

McMurray, J. et al., 2021. ORNL/SPR-2020/1865.

# Thermophysical Modeling

- Provides multicomponent data for reactor modeling

**Redlich-Kister expansion density, viscosity and thermal conductivity:**

$$\rho_{mix} = \frac{x_A MW_A + x_B MW_B}{\frac{x_A MW_A}{\rho_A} + \frac{x_B MW_B}{\rho_B}} + x_A x_B \left(L_1 + (x_A - x_B) L_2 + (x_A - x_B)^2\ L_3 + \cdots\right)$$

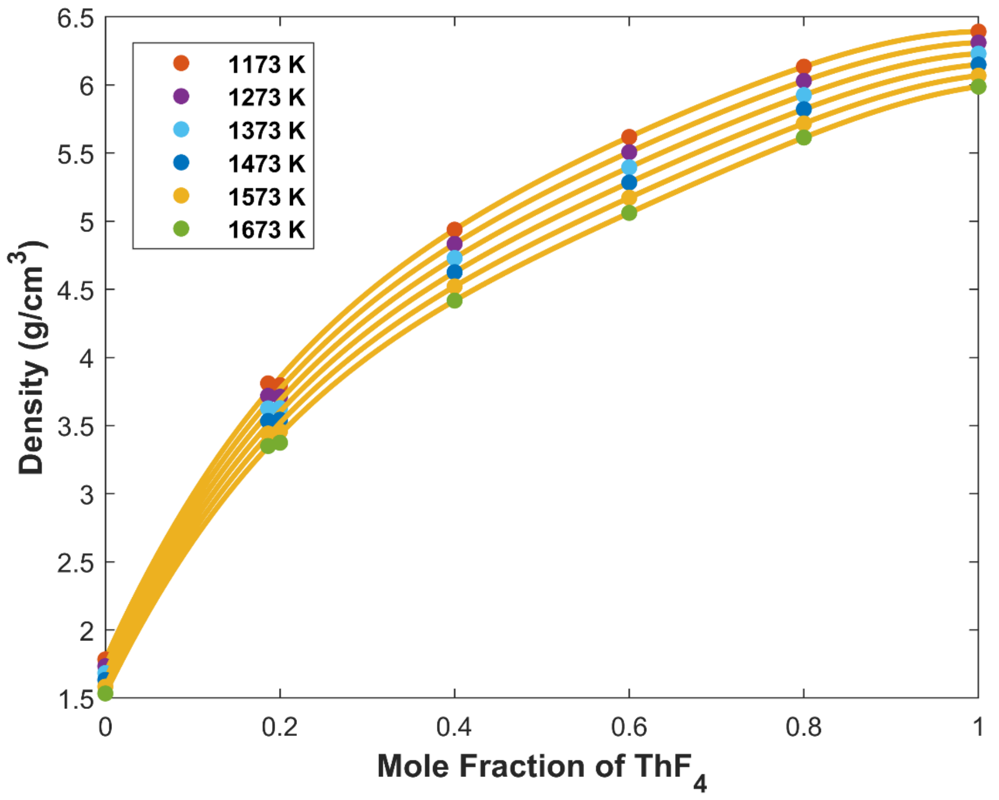
$$\log \mu_{mix} = x_A \log \mu_\mathrm{A} + x_B \log \mu_\mathrm{B} + x_A x_B \left(L_1 + (x_A - x_B) L_2 + (x_A - x_B)^2\ L_3 + \cdots\right)$$

$$\lambda_{mix} = x_A \lambda_A + x_B \lambda_B + x_A x_B (L_1 + (x_A - x_B) L_2 + \cdots)$$

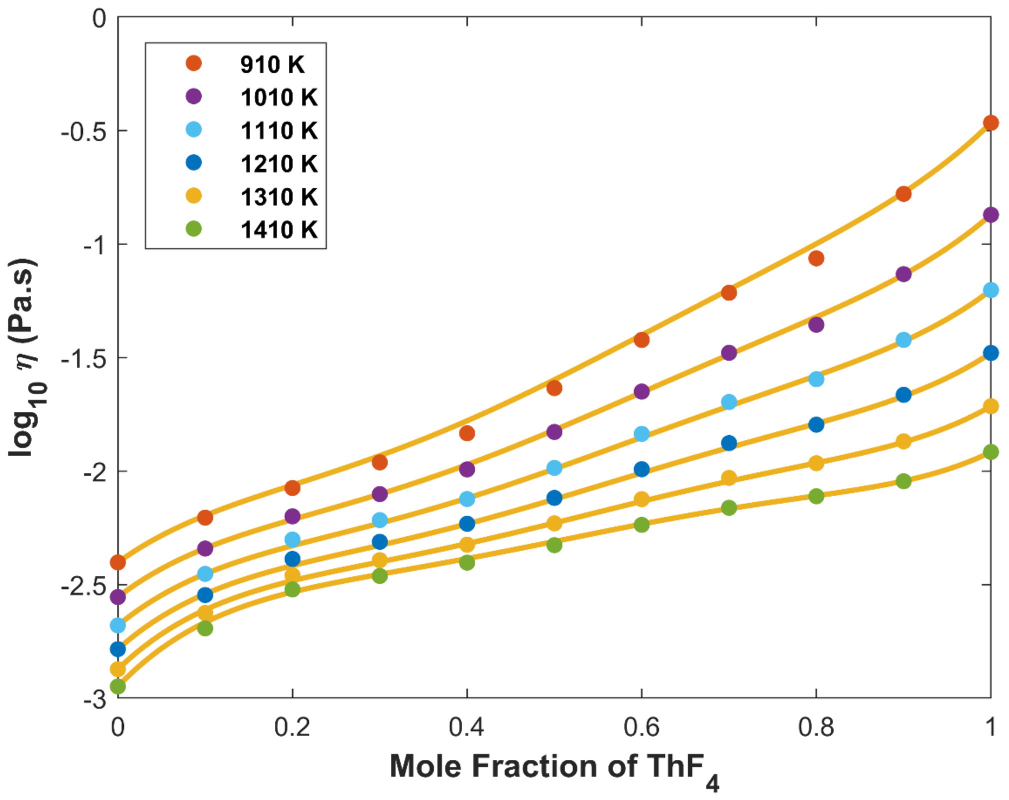
$$L_i = A_i + B_i T$$

Redlich, O.; Kister, A. T.. *Ind. Eng. Chem.* **1948**, *40* (2), 345–348.

# LiF-$ThF_4$ Molten Salt Results



**LiF-$ThF_4$ molten salt system density model**

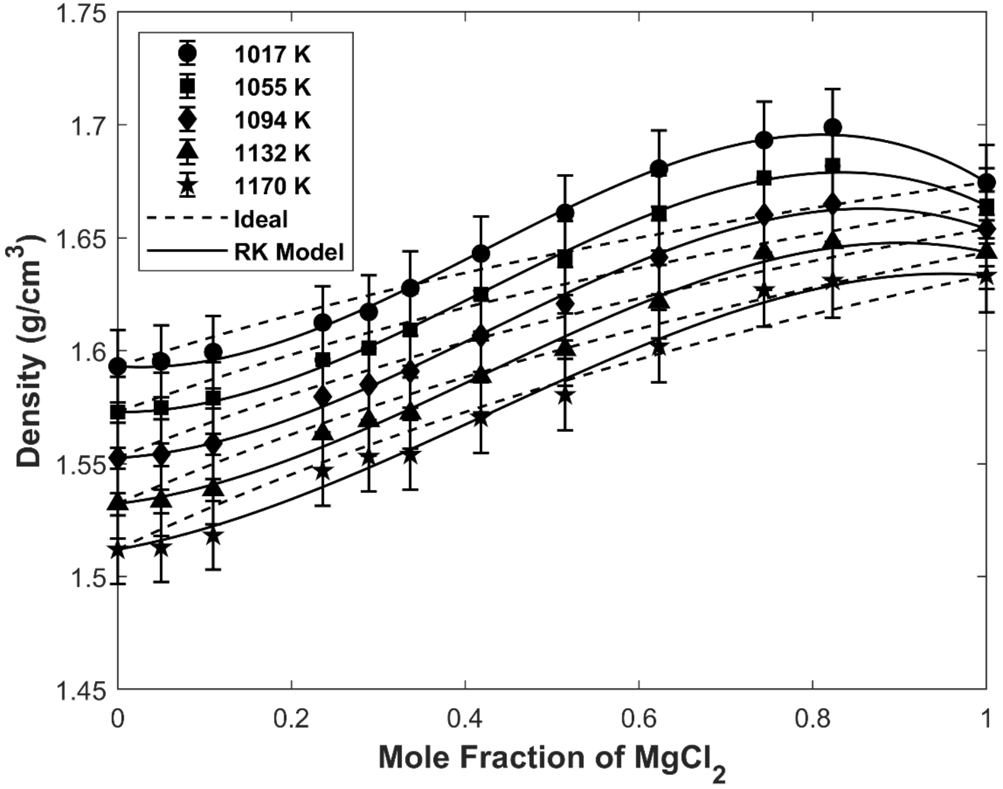


**LiF-$ThF_4$ molten salt system viscosity model**

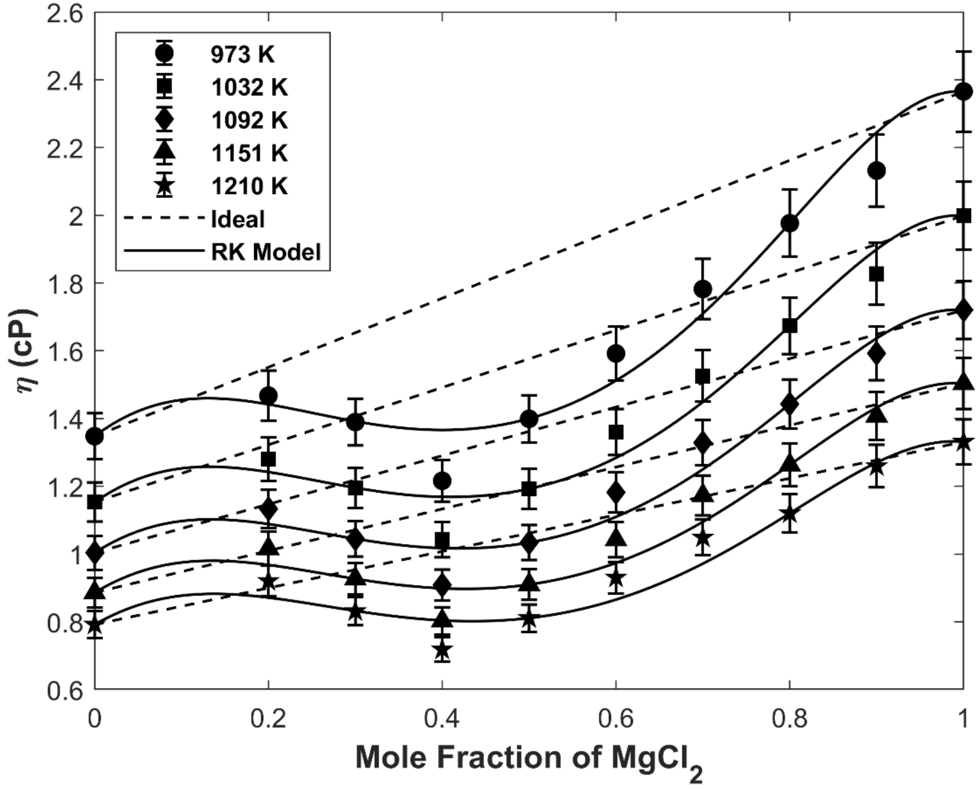
Hill, D. G. et al. *J. Inorg. Nucl. Chem.* **1967**, 29 (1), 241–243.

Chervinskii, Y. F. et al. I. *Zhurnal Fiz. Khimii* **1982**, *56* (8), 1946–1949.

# $MgCl_2$-NaCl Molten Salt Results



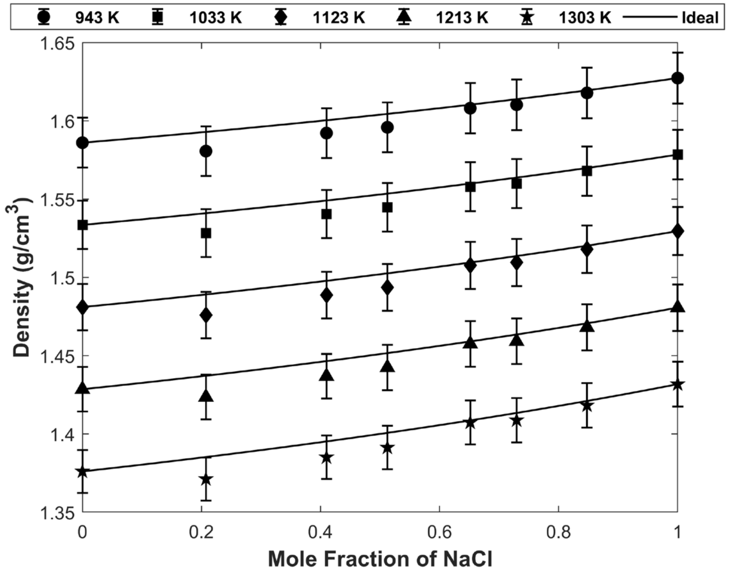
**$MgCl_2$-NACl molten salt system <u>density</u> model**



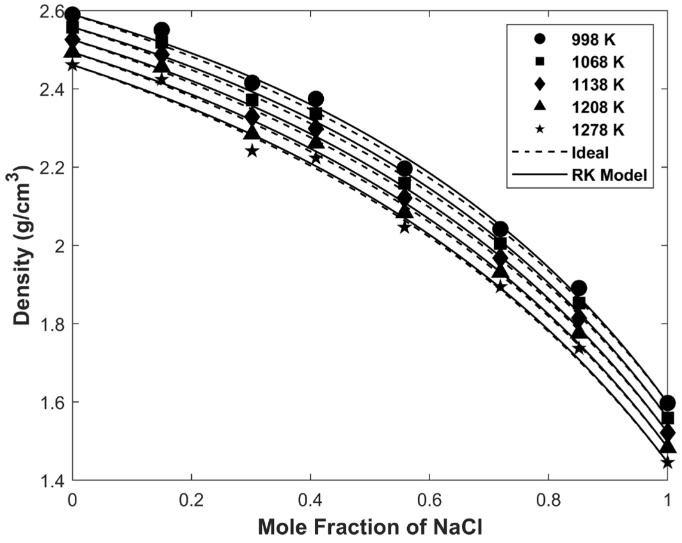
**$MgCl_2$-NACl molten salt system <u>viscosity</u> model**

Bondarenko, N. V., and Strelets, Kh. L., J. Appl. Chem. (USSR), 38, 1254 (1965).
Lillebuen, B., Ph.D. Thesis, The Technical University of Norway, Trondheim, Norway, (1969).

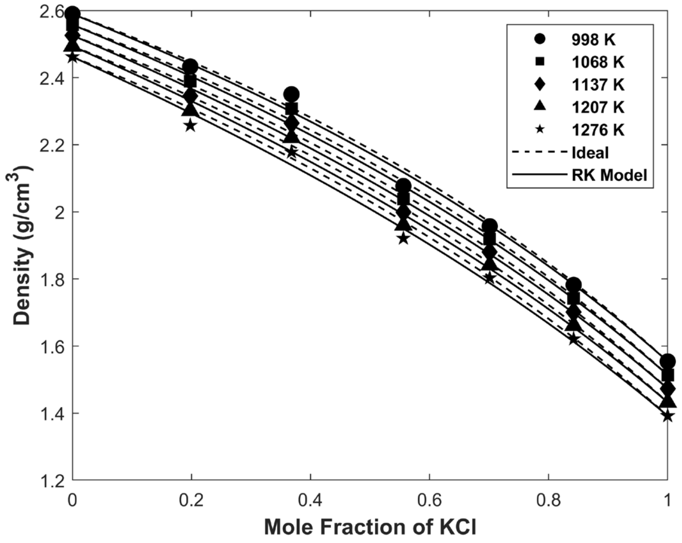
# Density of NaCl-KCl-$YCl_3$ Molten Salts Results



NaCl-KCl molten density: ideal behavior within 1%



NaCl-$YCl_3$ molten density: RK 1st order



KCl-$YCl_3$ molten density: RK 1st order

- $YCl_3$well-known rare-earth fission products in MSRs
- All three binary liquid mixtures behave close-to-ideal in density

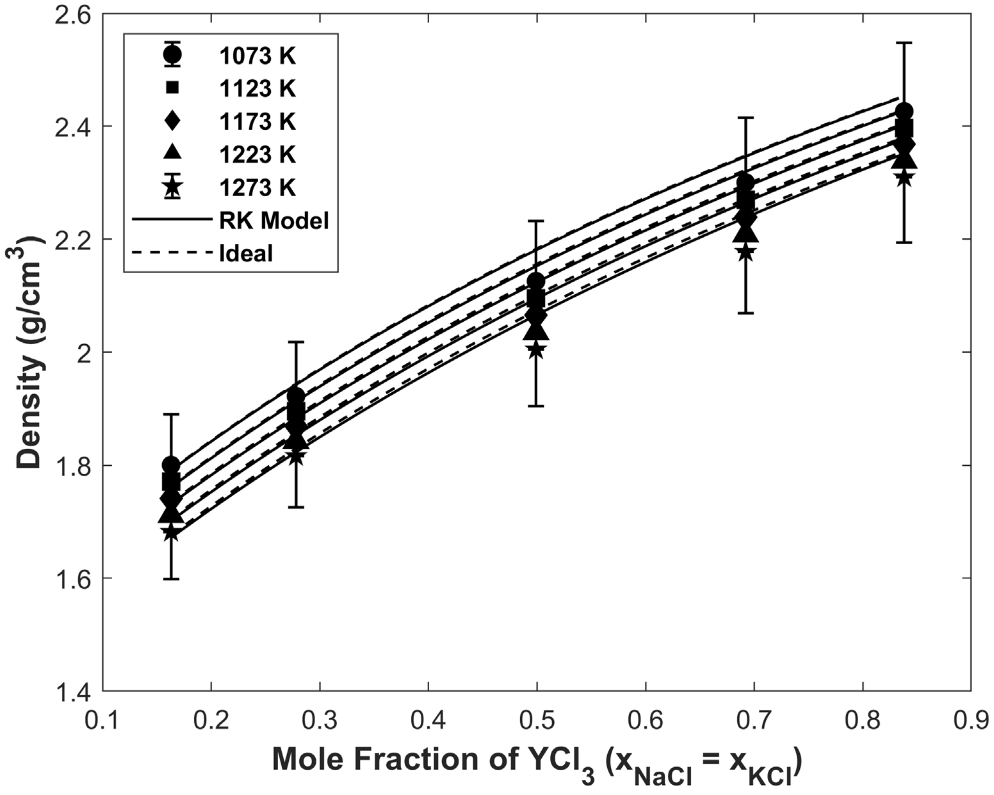
Agca, C.; McMurray, J. W. *Chem. Eng. Sci.* **2022**, *247*, 117086.

Mochinaga, J., Irisawa, K., 1974. Bull. Chem. Soc. Jpn. 47, 364–367.

Van Artsdalen, E.R., Yaffe, I.S., 1955. J. Phys. Chem. 59, 118–127.

# Density of NaCl-KCl-YCl$_3$ Molten Salts Results

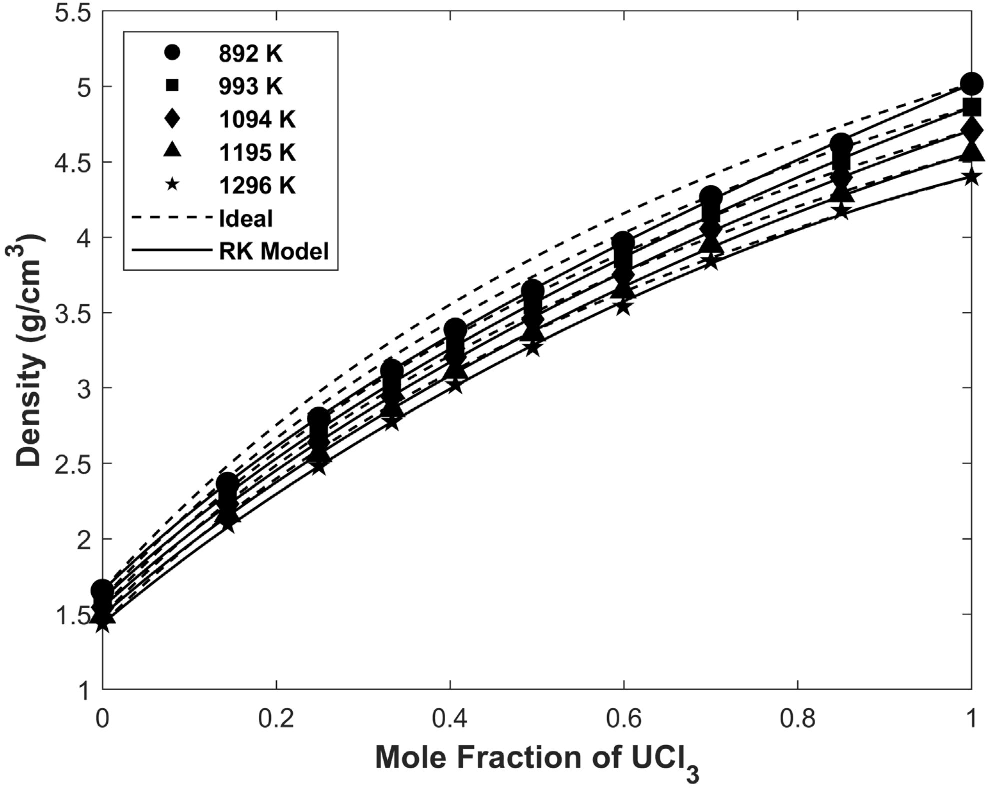
- Muggianu interpolation from binary molten salt interaction parameters
- Good agreement within 2-3%
- Ideal-like behavior for engineering design purposes



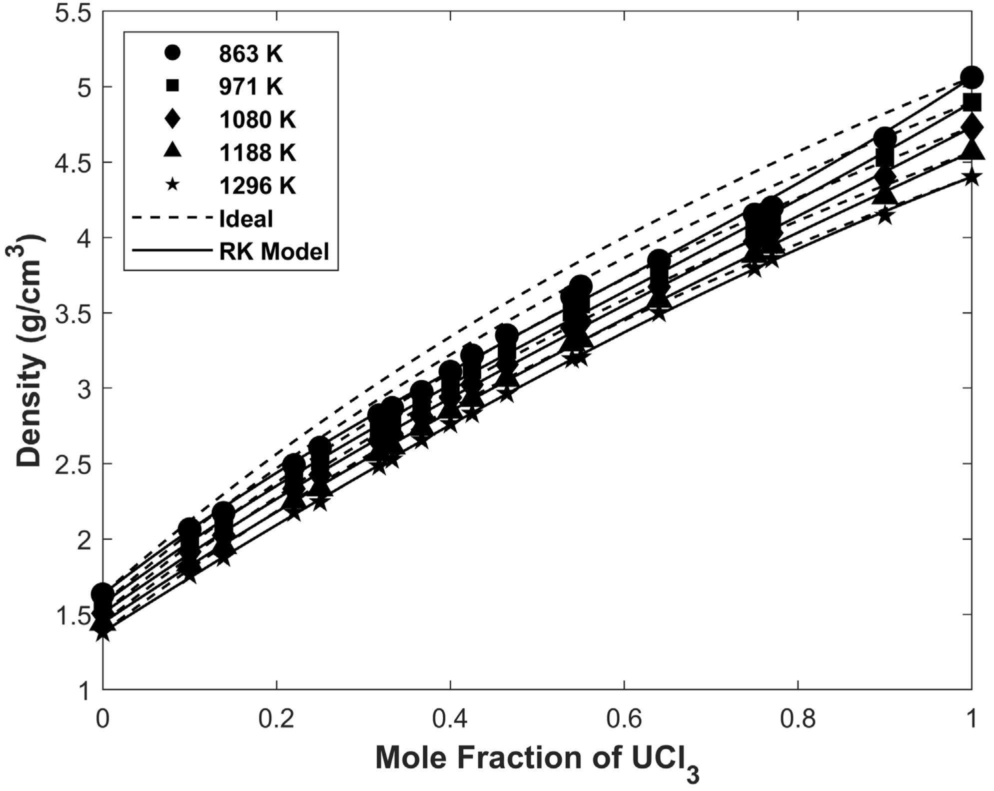
$$\rho_{ex} = x_A x_B \sum_{j=1}^{n} L_j (x_A - x_B)^{j-1} + x_A x_C \sum_{j=1}^{n} L_j (x_A - x_C)^{j-1} + x_B x_C \sum_{j=1}^{n} L_j (x_B - x_C)^{j-1}$$

Agca, C.; McMurray, J. W. *Chem. Eng. Sci.* **2022**, *247*, 117086.
Muggianu, Y.-M. et al., 1975. J. Chim. Phys. 72, 83–88.
Mochinaga, J., Irisawa, K., 1974. Bull. Chem. Soc. Jpn. 47, 364–367.

# Density of NaCl-KCl-$UCl_3$ Molten Salt Results



**NaCl-$UCl_3$ molten salt density: RK 2nd order**



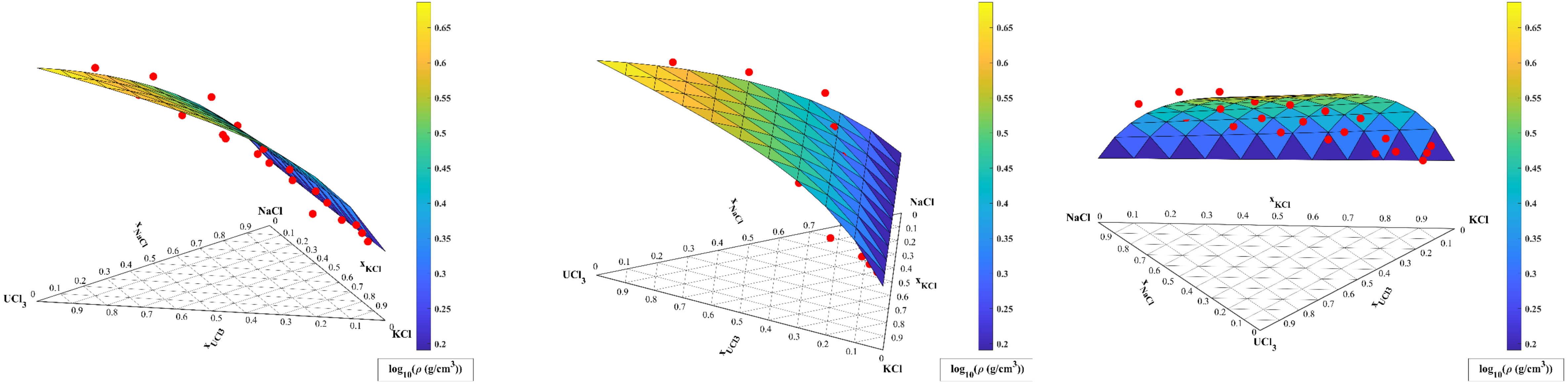
**KCl-$UCl_3$ molten salt density: RK 2nd order**

Agca, C.; McMurray, J. W. *Chem. Eng. Sci.* **2022**, *247*, 117086.

Desyatnik, V. N. et al. Sov. At. Energy 1975, 39 (1), 649–651.

Desyatnik, V. N. et al. Zhurnal Fiz. khimii 1976, 50 (10), 2522–2525.

# 3D visualization of the Density of NaCl-KCl-UCl$_3$



- NaCl-KCl-UCl$_3$ system at 1000 K shows a good agreement with Katyshev et al. (1983)

Agca, C.; McMurray, J. W. *Chem. Eng. Sci.* **2022**, *247*, 117086.

Katyshev, S.F. et al. 1983. J. Appl. Chem. USSR 56, 2000–2002.

# Molten Salt Thermophysical Properties API

- Under active development
- Provides a stable C++ interface for obtaining supported properties (density, viscosity, heat capacity, and thermal conductivity)
  - Can be extended to provide access to alternate and/or additional data models without affecting client codes.
- Seeks to provide results which mirror experiment while being robust in the absence of data.
  - Falls back on ideal mixing
- Support for standalone use provided via python bindings
  - Could be extended to additional bindings

Henderson, S. et al. *Saline: An API for Thermophysical Properties, ORNL/TM-2021/2239*; 2021.

# Conclusions and Future Work

- A framework has been developed and path forward proposed for multicomponent salt thermal property modeling
- Fundamental pure component and binary mixture data are used as inputs to populate the MSTDB
- Key data gaps have been identified and systems for computational and experimental studies have been selected
- An API has been developed for coupling the MSTDB-TP to NEAMS and other codes for multiphysics modeling and simulation

# Questions?

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