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Thermal Properties Measurements of Molten Salts At Argonne National Laboratory

MSR Developer Conference 2022

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Molten Salt Reactor PROGRAM

Objective: Provide the data necessary to build a FOAK MSR by 2035

Targeting molten salt reactor developer needs to support design, licensing and operation of molten salt reactors

- **Thermochemical and thermophysical properties of molten salts**
  - Generating quality data to predict the behavior of molten salts during normal and transient operations (Melissa Rose)
- Real-time chemistry monitoring and accountancy of materials in MSRs
  - Developing accurate sensors resistant to radiation damage and corrosive molten salt environments (Nathan Hoyt)
- Accident scenario analyses supporting the licensing process
  - Generating data needed to simulate salt spills, spreading behavior, and release of FPs as aerosols and vapor (Sara Thomas)

Generating Thermal Property Data

Predicting molten salt behavior during normal and transient conditions requires knowledge of property values over a range of temperatures and compositions

- Generating quality data for systems of interest to MSR developers for which limited or no data exists
  - Supporting development of the Molten Salt Thermal Database (MSTDB)

- Developing capabilities to measure salt property values under more extreme conditions relevant to MSRs (higher temperatures, more corrosive salts)

Measuring plutonium-bearing salts as well as binary and ternary uranium-bearing mixtures to expand the database of relevant mixtures available to developers

Laboratory Capabilities

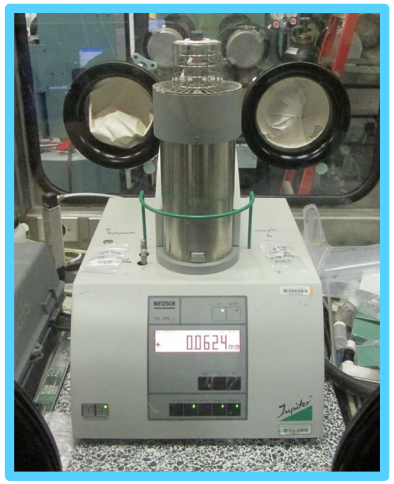
- Radiological facility housing purpose-built inert atmosphere gloveboxes used for experiments with actinides, beryllium and simulated fission products
  - Glovebox furnace wells from six to thirty-six inches with furnace capability to 800°C
  - Induction and resistance furnaces for higher temperature applications

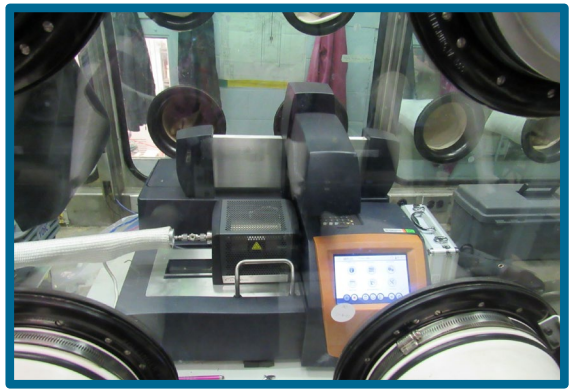
- Expertise and capabilities in areas essential to advancement of molten salt nuclear energy systems:
  - Thermophysical property measurements
  - Materials compatibility and corrosion studies
  - Electrochemical monitoring and control of salt chemistry and materials accountability
  - Linking understanding of fuel cycle chemistry and engineering

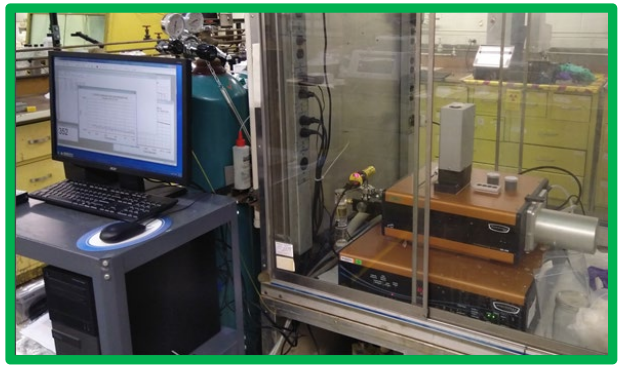
Thermophysics laboratory with equipment located in Ar-atmosphere radiological gloveboxes

Molten Salt Property Measurement capabilities at Argonne

Property	Method
Density, volumetric thermal expansion and surface tension	Archimedes method (in Ar-atmosphere rad glovebox)
Heat capacity, melting point, phase equilibria	Differential scanning calorimeter (DSC) (in Ar-atmosphere rad glovebox)
Viscosity	Rotating spindle viscometer (in Ar-atmosphere rad glovebox)
Thermal diffusivity & thermal conductivity	Laser flash analysis system (in rad hood with Ar purge or under vacuum)
Fission product & actinide solubility	Chemical analyses and DSC
Mass transfer diffusion coefficients	Restricted diffusion cells (in Ar-atmosphere rad glovebox)
Vapor Pressure	Coupled Thermogravimetric Analysis with Quadrupole Mass Spectrometry





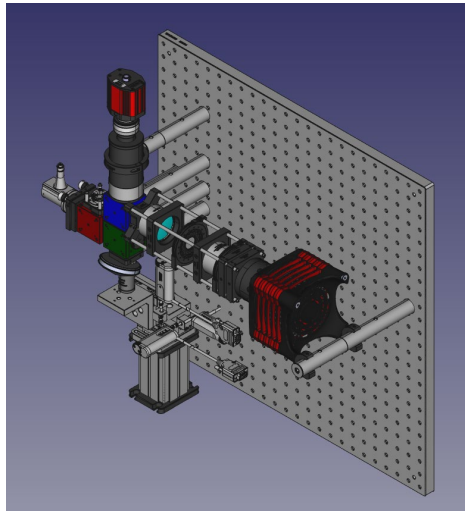


Molten Salt Chemical Analysis Capabilities

On-site analytical chemistry laboratory provides rapid turn-around molten salt analyses

Method	Compositional Information
ICP-OES	Elemental analysis ppm level
ICP-MS	Elemental analysis at <ppm level
XRD	Identification of crystalline phase composition
Alpha Spectroscopy	Identification and quantification of alpha-emitting isotopes
Gamma Spectroscopy	Identification and quantification of gamma-emitting isotopes
Liquid Scintillation Counting	Measurement of alpha/beta activity
Raman Spectroscopy	Measurement of speciation (vibrational modes of ionic clusters)
Inert gas fusion (LECO)	Quantification of C, S, O, N contaminants at <1 mg/g level

LECO measurement of oxide concentration in molten salt including beryllium salts

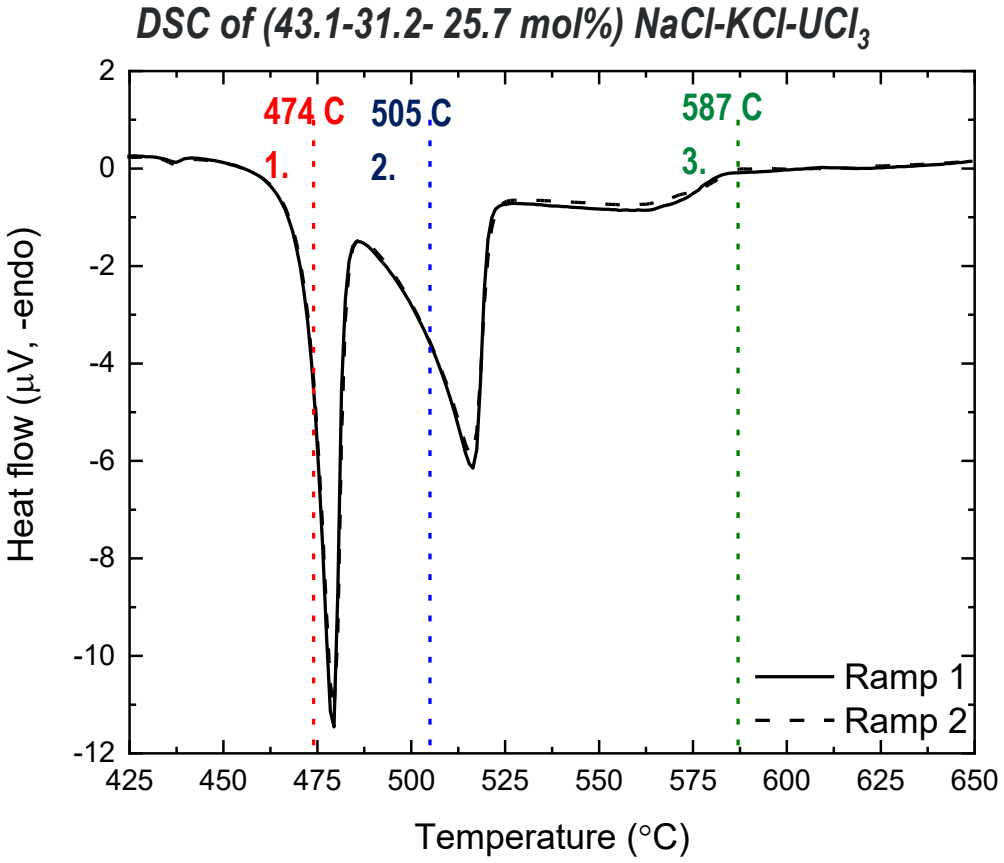


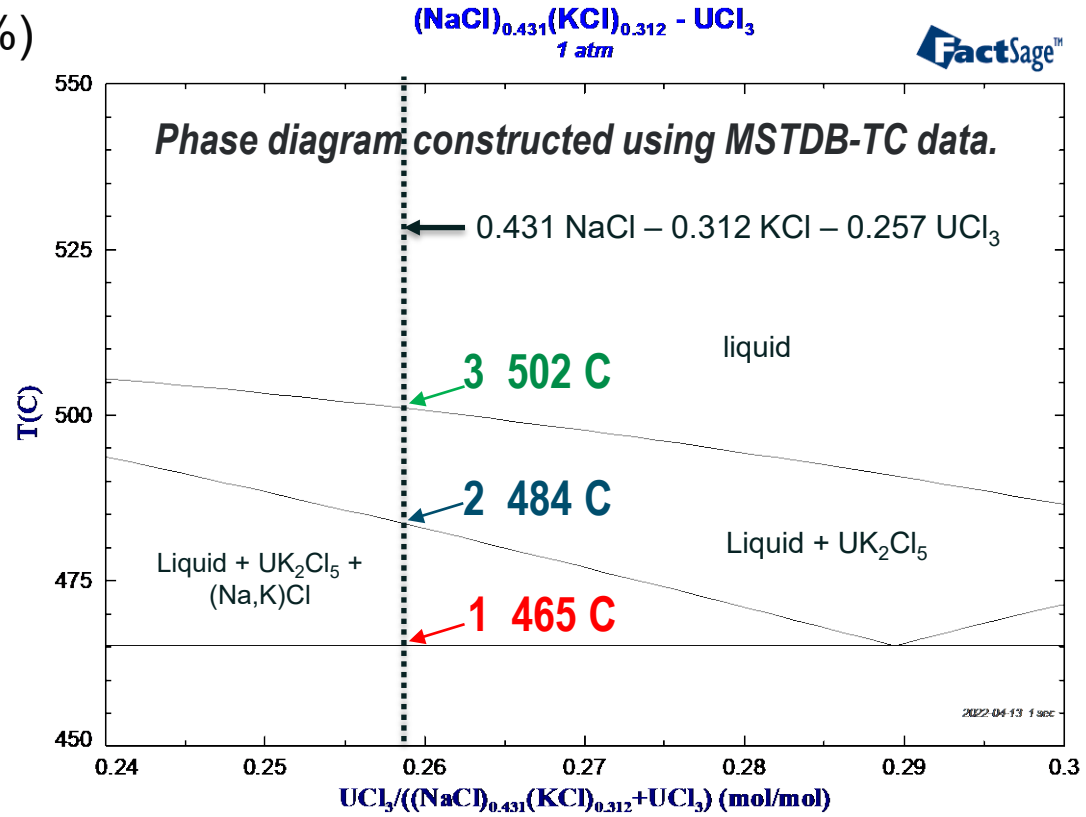
Raman spectroscopy of molten salts

- *Spectroscopy from ~15 to ~3500 cm^{-1}*
- *Portable and reconfigurable*
- *Microspectroscopy*

NaCl-KCl-UCl_3 measurements vs. modeling

- Measured the thermal properties of (43.1-31.2- 25.7 mol%) NaCl-KCl-UCl_3
- Use of values in MSTDB underpredicts liquidus temperature significantly



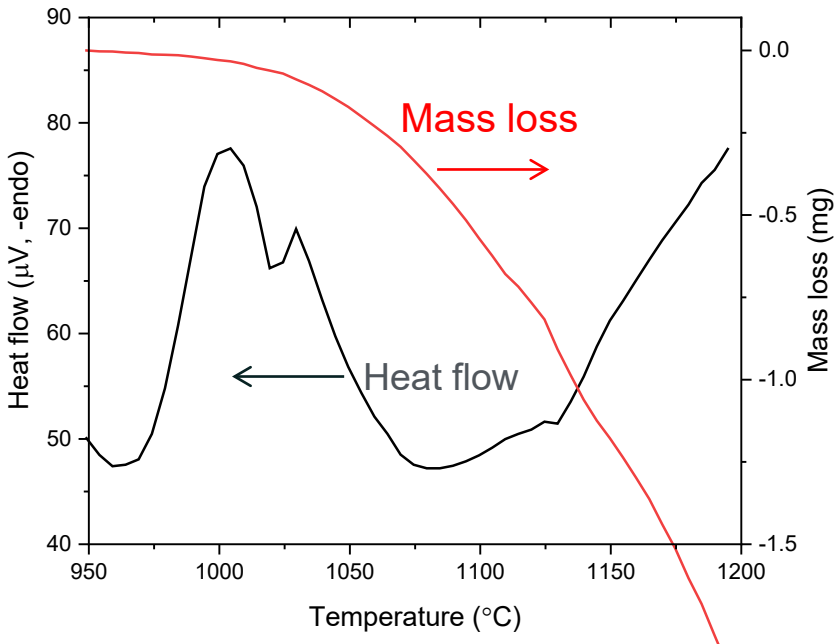


DSC Feature	Reaction	Measured Temp.	Predicted Temp.
1	Solid → Liquid +UK_2Cl_5 + (Na,K)Cl	474 ± 2 °C	465 °C
2	Melting (Na,K)Cl → Liquid + UK_2Cl_5	505 ± 2 °C	484 °C
3	Liquidus	587 ± 2 °C	502 °C

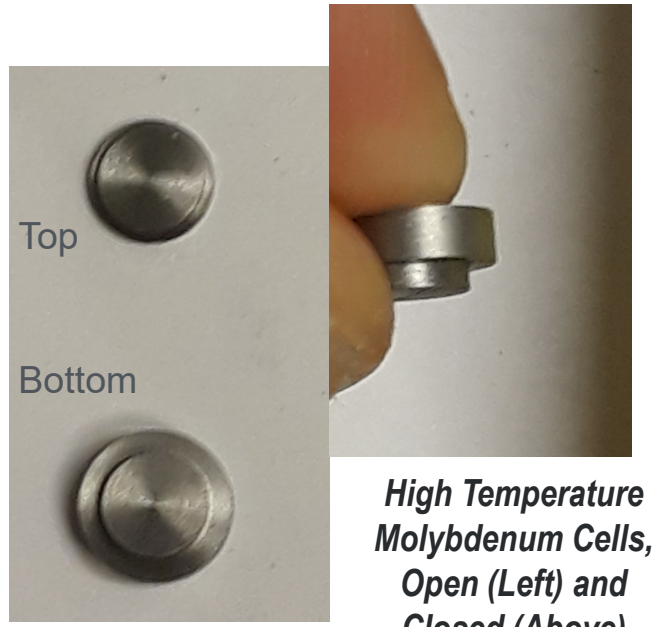
Enabling Measurements at High Temperature

- Sealable cells are required for high quality heat capacity measurements using DSC:
  - Developing robust mechanically sealable cells for use above 750 °C
- Cells must be inert to a variety of molten salts and retain malleability to be sealable
  - Ni and Mo of various thicknesses were tested for required shaping and sealing
  - Different annealing procedures were attempted and Ni and Mo were not found to be satisfactory
  - Next set of cells will be fabricated from Pt alloys

High Temperature Nickel Cells, Open (Left) and Sealed (Right)



Heat flow and mass loss curves of heating UF_4 in a closed but unsealed molybdenum cell

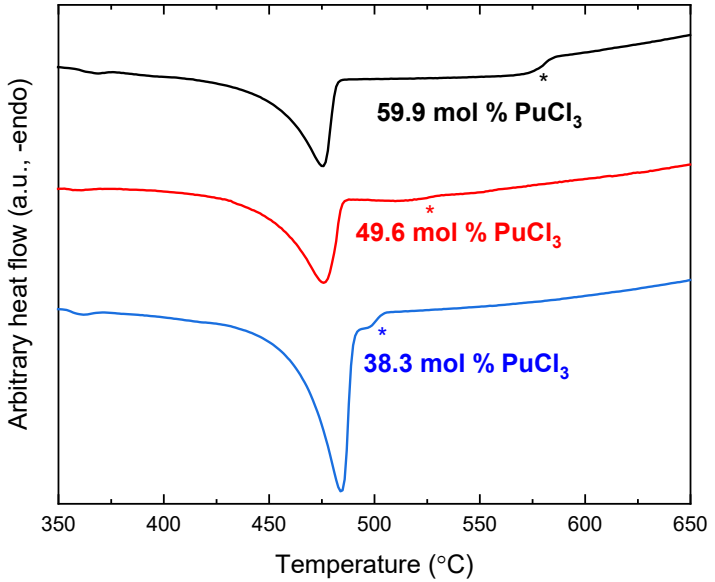


High Temperature Molybdenum Cells, Open (Left) and Closed (Above)

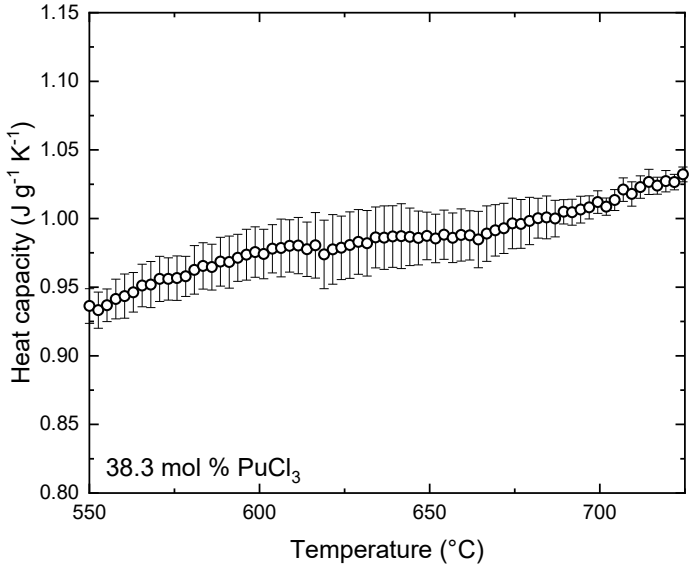
$NaCl\text{-}PuCl_3$ Measurements

The binary $NaCl\text{-}PuCl_3$ system was examined to support developer needs

- Few empirical investigations into the phase equilibria of this system exist
- Eutectic composition is likely between 36 and 38.3 mol % $PuCl_3$ based on published studies
- Phase equilibria measured for series of near-eutectic compositions by using DSC
  - 59.9, 49.6 and 38.3 mol % $PuCl_3$
  - Still measuring 37.4, 36, 30 and 20 mol % $PuCl_3$
- Heat Capacity of 36, 37,4 and 38.3 mol % $PuCl_3$ are being measured by DSC for both the solid and liquid phases



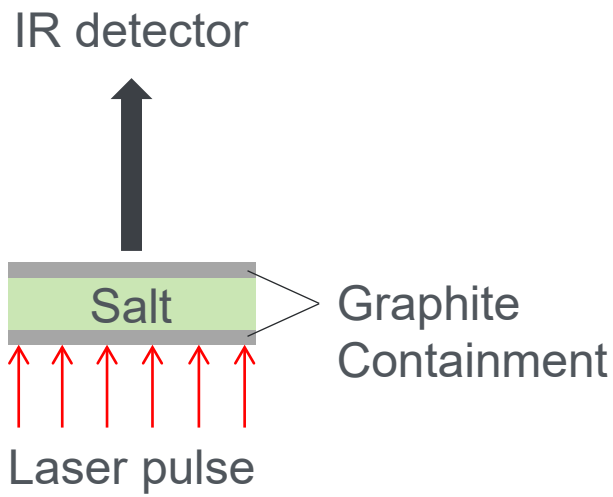
Measured thermal behaviors of three $NaCl\text{-}PuCl_3$ mixtures

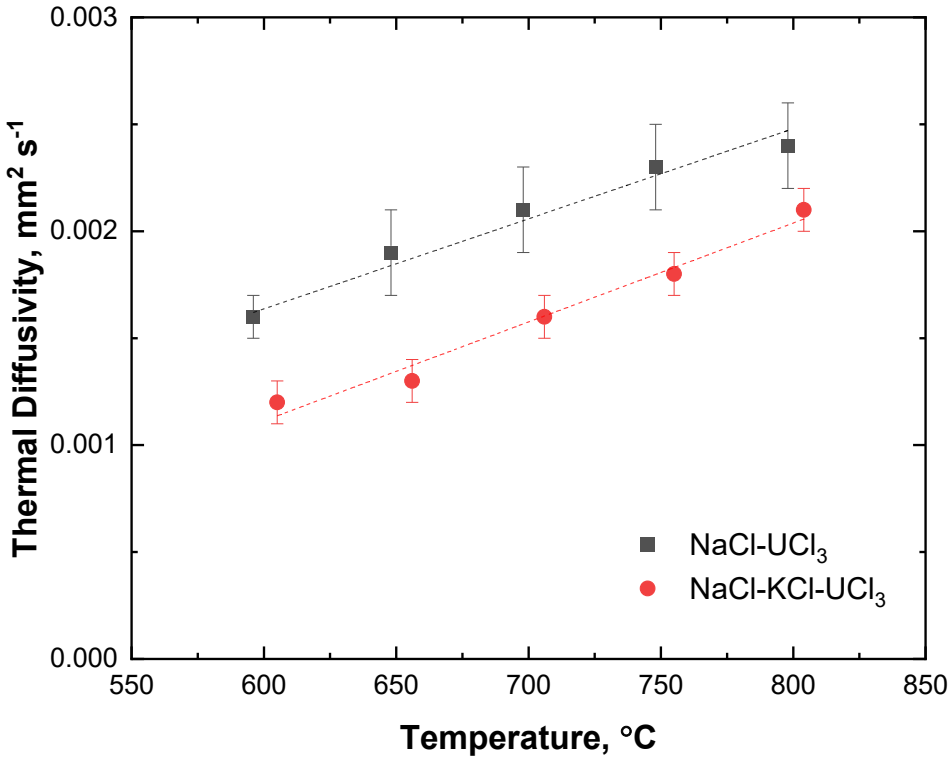


Average and one standard deviation of three measurements of liquid heat capacity of one sample of $NaCl$-38.3 mol % $PuCl_3$

Thermal Diffusivity Measurements of NaCl-KCl-UCl_3 System

- Thermal diffusivities of (43.1-31.2-25.7 mol%) NaCl-KCl-UCl_3 and (66-34 mol%) NaCl-UCl_3 measured using laser flash analyzer
- A laser pulse is applied to one surface of a sample and the temperature response vs time at the other side is measured
- Graphite sample cells are used to contain salts

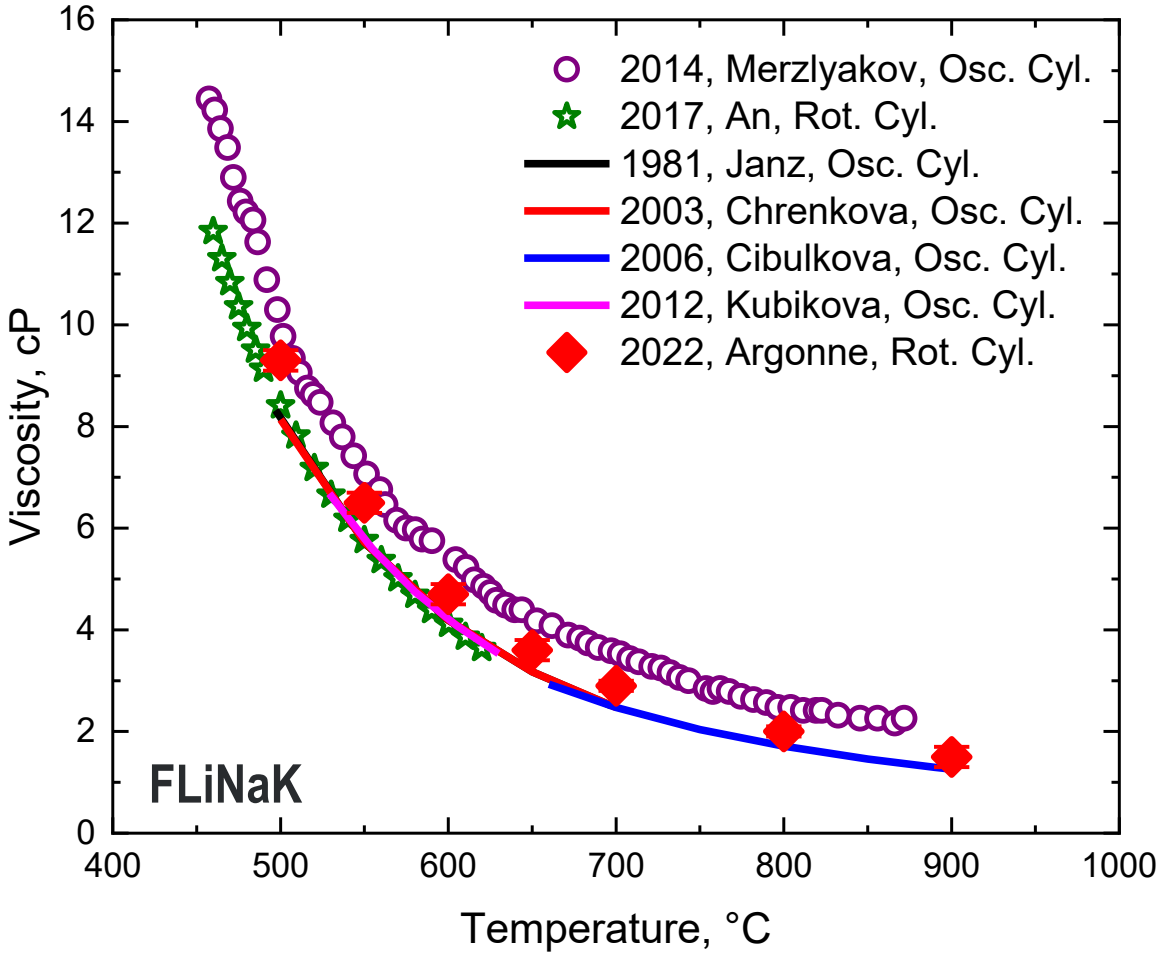




Thermal Diffusivity Measurements of NaCl-UCl_3 and NaCl-KCl-UCl_3. Average and standard deviation of three measurements at each temperature are shown.

Viscosity Measurements Using a Rotational Viscometer

- A spindle is submerged in a molten salt and the torque required to maintain a constant rotational velocity is measured.
- Parameter values affecting measurements:
  - Temperature stability
  - Volume of fluid above spindle
  - Turbulence in fluid
  - Impurities (e.g., undissolved solids)
- Have measured viscosities of reference salts and actinide-bearing chloride and fluoride salts for private sponsors
  - Determined precision and accuracy using reference fluids



Viscosity measurements of FLiNaK compared to literature data. Measurements are average and one standard deviation of 15 measurements at each temperature

Summary

Argonne is generating high quality property data to enable a FOAK MSR by 2035

- Generating high quality data for NaCl-UCl_3, NaCl-KCl-UCl_3 and NaCl-$PuCl_3$ systems to fill gaps in the MSTDB
- Developing high temperature mechanically sealable cells for use in thermal analysis by differential scanning calorimetry
- Comparing measured properties to model predictions using MSTDB data.

Acknowledgements

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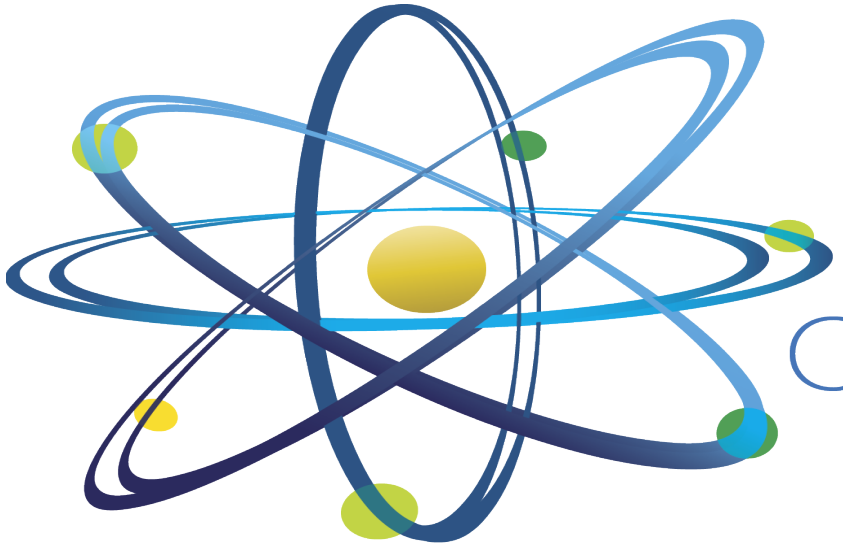
Questions



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