Mixing enthalpy of LnCl$_3$ in molten chloride salts

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Molten salt research – what high T calorimetry can help?

Measured enthalpy interaction parameter (related to $\Delta H_{\text{mix}}$) in selected alkali fluoride – rare earth fluoride molten mixture\(^1\)

- Cross-check and constrain the mixing behaviors predicted by models refined from XAFS/scattering, improving force field used.
- The experimental measured interaction parameter (and formation enthalpy of solids) will benchmark CALPHAD (or AIMD, ML) modeling.
- (Enthalpy of mixing) of molten salts at high T
- (Enthalpy of formation) of solidified intermediate salt components.
- (Enthalpy of reaction) of trace fission products or corrosion products

Optimize phase diagram to be better predictive of salt behaviors

\(^1\) Hong and Kleppa, J. Phys. Chem. 1979, 83, 2589
Calorimetry Capability at WSU

**Basement lab (B21), located in a Nuclear Reactor building**
- Temperature fluctuation < 0.5 °C
- Equipped with a rad glove-box for handling Pu (powder processing and pelletizing)

- Large quantity of $^{232}$Th, $^{238}$U;
- Moderate amounts of Np, Pu, (Am, Cm, Cf and other transuranium) (~ 100 Ci/yr)

**Produced enthalpy data:**
\[ \Delta H_{ds} = \Delta H_{hc} + \Delta H_{rxn} + \Delta H_{soln} \]

- Isoperibol Type, 500 ~ 1000 °C
- Determine heats of reactions
- Refractory, volatile-bearing, air-sensitive, molten salts.
Experimental determination of LaCl$_3$ mixing in LiCl-KCl eutectic melt

**Preliminary goals:**

1) Determine enthalpy of mixing within the LaCl$_3$:LiCl-KCl system at 600 C.

2) Extract the interaction parameters within the solubility region of interest
Loading LaCl$_3$ under inert atmosphere  
$< 0.5$ ppm O$_2$, $<0.5$ ppm H$_2$O

Airtight custom-built droppers

KCl-LiCl melt

Steady Ar head space

Drop LaCl$_3$ pellet into molten KCl-LiCl eutectic

General procedure for handling chloride salts for calorimetry
Two Methods: Continuous Drop Method and Discrete Drop Method (Physical Mixture)

Continuous Drop Method

1. Pre-melt LiCl-KCl eutectic in crucible
2. Drop LaCl$_3$ pellets from RT into the eutectic
   - 4 trials conducted
   - 3 using fused LaCl$_3$ pellet, 1 using pressed powder pellets

Discrete Drop Method

1. Pre-melt LiCl-KCl eutectic in the glovebox furnace
2. Physically mix specified ratios of LaCl$_3$ with LiCl-KCl
3. Make pellets
4. Drop into an empty Ni crucible
   - Allows repeated drops = error analysis from a single trial
   - Time consuming and relies more on accessory thermochemical data

\[ \Delta H_{\text{sol}*} = \Delta H_{\text{cp}} + \Delta H_{\text{fuss}} + \Delta H_{\text{mix}} \]
Results from the two methods

\[ \Delta H_{\text{mix}} = [x \ \Omega_1 + (1-x) \ \Omega_2] \cdot x \cdot (1-x) \]

- \( \Delta H_{\text{mix}} \) max at \( \sim 19 \) mol. % LaCl\(_3\)
- Fit with 2 interaction parameters

\[ \lambda = \Delta H_{\text{mix}} / [x \cdot (1-x)] \]

- Strong stabilizing interaction in alkali rich region
- General agreement between all trials
Results from the two methods

Polynomial fit utilized:

$$\lambda = a \ (T, P, X) + b \ (T, P, X) \cdot X + c \ (T, P, X) \cdot X^2$$

- $a = -25$ kJ/mol
- $b = 68$ kJ/mol
- $c = -30$ kJ/mol

Dispersion interaction between cations

Coulombic and polarization energy
Data summary

\[ \Delta H_{\text{mix}} = \Delta H_{\text{mix}}^C + \Delta H_{\text{mix}}^K \]

\[ \lambda = \lambda^C + \lambda_{\text{mix}}^K \]
New Approaches to Thermal Conductivity and Viscosity Measurements in Molten Salts

Alex Bataller, Assistant Professor
Department of Nuclear Engineering
North Carolina State University

Molten Salt Thermal Properties Working Group
Virtual Workshop
Tuesday, November 16th, 2021
Host: University of South Carolina
Micrometrology of Molten Salts

Thermoreflectance
Thermal Conductivity and Heat Capacity

Brownian Motion
Viscosity

Syed Rizvi, PhD Student

Hayden Bland, Undergrad
Thermal Conductivity: Measurement Challenges

“The thermal conductivity of molten salt is the most difficult fluid property to measure, and it has led to the greatest amount of confusion and error in heat-transfer calculations.”


Why?

• Corrosion
  • Material selection
  • Inert atmosphere

• High temperature operation
  • Heating/cooling/insulation design
  • Temperature uniformity

• High temperature heat transfer
  • Convection
  • Thermal radiation

Parallel Plate Heating

Conduction: $\phi_c = k \frac{\Delta T}{\Delta x}$

Radiation: $\phi_r = \varepsilon \sigma \left( (T_0 + \Delta T)^4 - T_0^4 \right) \sim 4 \varepsilon \sigma \Delta T T_0^3$

Thermal Conductivity Methods

**Variable Gap**


**3-ω**


**Transmit Hot Wire**

**Laser Flash**

Thermoreflectance

Photothermal Technique Creates Strong Thermal Gradient

Molten Salt

Gold Transducer

Fused Silica Window

Heat Transfer

Photothermal “Pump”

Reflective “Probe”
1. Optical method (non-invasive, *in situ*, material independent)
2. Simultaneous measurements of heat capacity, thermal conductivity, and interfacial thermal conductance
3. Strong thermal gradients; radiation is relatively weak and convection is suppressed near the boundary
Thermoreflectance

Well-defined thermal boundary value problem governed by Fourier’s law:

$$C \frac{\partial T}{\partial t} = k \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + k \frac{\partial^2 T}{\partial z^2}$$

Analytic solution is possible for general n-layer system!

Hankel & Fourier transform,

$$\frac{\partial^2 \tilde{T}}{\partial z^2} = q \tilde{T}; \quad \tilde{T}(r', z, \omega) = E e^{qz} + F e^{-qz}$$

$$q^2 = r'^2 + i\omega C/k$$

For an n-layer system,

$$\begin{bmatrix} \tilde{T} \\ \tilde{Q} \end{bmatrix}_{i=n, z=d_n} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} \tilde{T} \\ \tilde{Q} \end{bmatrix}_{i=1, z=0}$$

where the matrix coefficients are given by the heat capacity and thermal conductivity of the bulk materials and the interfacial thermal conductance between layers.

After applying boundary conditions, the thermal response of the system is obtained compared to the probe reflectivity.
Thermoreflectance

Diagram showing a schematic of a thermoreflectance experiment setup. The setup includes a femtosecond laser, an isolator, a polarizing beam splitter, a BBO crystal, a 400 nm filter, a flip mirror, a photodiode, an EOM, and a CCD camera. The setup is connected to various optical components such as a beam expander and a beam reducer. The samples are mounted on a 10X microscope with a cold mirror and a beam splitter. The optical delay line is also shown.

Images of the experimental setup are also included, showing the physical arrangement of the equipment.
Thermoreflectance - Air

FDTR

![Frequency vs. Amplitude for FDTR](image1)

![Phase vs. Frequency for FDTR](image2)

TDTR

![Amplitude vs. Time for TDTR](image3)

![Phase vs. Time for TDTR](image4)
Simultaneous $k$ and $C$

Absorptive Pump  Reflective Probe

Radial Wave

Gold Film

Molten Salt

$L_{\text{radial}} \gg \frac{1}{4}w$

Thermal Wavelength

$L = \sqrt{\frac{2k}{\omega C}}$

$L_{\text{plane}} \ll \frac{1}{4}w$

Glass-Gold-Water

Amplitude Sensitivity

$k$-sensitive

$\sqrt{kC}$-sensitive

$log f_0$(MHz)
Salt is a Lousy Thermal Conductor

**Supported**

- Molten Salt
- Gold Film
- Quartz Substrate

**Free-Standing**

- Molten Salt
- Gold Film

**Symbols and Equations**

- \( \kappa_{gs}, C_{gs} \)
- \( G_{gs} \)
- \( \kappa_g, C_g, d_g \)
Doubling Sensitivity

Supported

Free-Standing

But how do we make free-standing 100 nm gold films??
Free-Standing Gold

TEM grids on floating gold

Molten salt furnace
• Fundamental fluid property that describes the resistance to flow

• Thermal energy transport

• Large change with eutectic composition

• Molten salts ~ 1-10x water
Viscosity: Go with the Flow…

• Usually, viscosity measurement techniques must establish a well-defined and controlled fluid flow.

• An excitation/motion establishes relative flow between a macroscopic object and the liquid:
  – Oscillation method
  – Vibration method
  – Rotating cylinder
  – Falling ball

Q: Can viscosity be measured without flow??
Microrheology

In 1908, Jean Perrin studied Brownian motion and verified Einstein’s predictions (Avogadro's number and molecular size) 1926 Nobel Prize in Physics

Einstein’s thesis 1905:
“A New Determination of Molecular Dimensions”

Microrheology with optical tweezers†

Alison Yao,⁎ Manlio Tassieri,⁎ Miles Padgett and Jonathan Cooper⁎⁎

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First published as an Advance Article on the web 15th June 2009
DOI: 10.1039/b907992k

Microrheology is the study of the flow of materials over small scales. It is of particular interest to those involved with investigations of fluid properties within Lab-on-a-Chip structures or within other micron-scale environments. The article briefly reviews existing active and passive methods used in the study of fluids. It then explores in greater detail the use of optical tweezers as an emerging method to investigate rheological phenomena, including, for example, viscosity and viscoelasticity, as well as the related topic of flow. The article also describes, briefly, potential future applications of this topic, in the fields of biological measurement, in general, and Lab-on-a-Chip, in particular.

Measuring Boltzmann’s constant through holographic video microscopy of a single colloidal sphere

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(Received 21 June 2013; accepted 15 October 2013)

The trajectory of a colloidal sphere diffusing in water records a history of the random forces exerted on the sphere by thermally driven fluctuations in the suspending fluid. The trajectory therefore can be used to characterize the spectrum of thermal fluctuations and thus to obtain an estimate for Boltzmann’s constant. We demonstrate how to use holographic video microscopy to track a colloidal sphere’s three-dimensional motions with nanometer precision while simultaneously measuring its radius to within a few nanometers. The combination of tracking and characterization data reliably yields Boltzmann’s constant to within two percent and also provides the basis for many other useful and interesting measurements in statistical physics, physical chemistry, and materials science.

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[http://dx.doi.org/10.1119/1.4827275]
Optical Microscope
Viscosity - Water

58 fps, 10 ms exposure, 1.7 μm diameter, 1000 frames
Viscosity - Water

- For each relative time between frames (“t”), displacements between positions are acquired by fitting to 2D gaussians
- Displacements in both x and y are placed into a histogram over ~10 runs
- Gaussian fits are made for each “t”; $\sigma^2 = \langle \Delta x^2 \rangle - \langle \Delta x \rangle^2 = \langle \Delta x^2 \rangle$
Viscosity - Water

\[ D = 0.2144 \pm 0.0003 \, \mu m^2 \, s^{-1} \]
\[ \eta = 1.187 \pm 0.002 \, cP \]
Future Work: Molten Salt

Challenges: Thermal uniformity and reducing fluid flow

1. High thermal conductivity materials in furnace for uniformity (e.g., diamond)
2. Thin cell design features a multi-step procedure for eliminating bubbles and reducing fluid flow:
   a. Fill system with solid salt and pump down to vacuum
   b. Apply heat to melting point
   c. Apply Ar overhead pressure to push fluid into void spaces
Future Work: Holography

Improvements to particle tracking will be provided by laser video holography, whose interference patterns will be fit to Lorenz-Mie theory yielding:

1. Particle’s position in “z” 50% more data per acquisition
2. The particle radius Polydisperse spheres
2. ~5x faster frame rates Reduction of flow contribution

Models for Simple Salts

• Simple molten salts are, to 1st order, rigid ion spheres (RIM)

• Largely vibrational heat transfer
  — Large thermal to mass diffusivity ratio
  — Lorenz ratio ($\lambda/\sigma T$) is not constant and 100s of times larger than in metals
  — Small change in thermal conductivity across melting transition

• Early model example: Rao (1941) assumed vibrations from a quasi-crystalline fluid (cubic lattice) analyzes vibrational heat flow using the Lindeman criteria,

$$k = C \left( \frac{n^{4/3}T_m}{M} \right)^{1/2}$$
Molecular Dynamics

- Molecular dynamics (MD) simulations to determine kinetics and thermodynamic properties
- DFT calculates the electronic ground state of a given configuration and composition, from there the interaction potential between ions are parameterized (e.g., PIM)
- Thermal conductivity can be extracted from MD simulations with sufficient runtimes using the Green-Kubo relation,

\[
\lambda = \frac{1}{T^2} \left( L_{EE} - \frac{L_{EZ}^2}{L_{ZZ}} \right),
\]

\[
L_{a,b} = \frac{1}{3k_B V} \int_0^\infty \langle j_a(t)j_b(0) \rangle dt
\]

where \( j \) is the energy and charge current.

THERMAL CONDUCTIVITY PROBES FOR MOLTEN SALTS

Troy Munro
Brigham Young University
Nuclear Research at BYU

BYU Nuclear Research Group (NRG)

- Material Science
  - Nuclear Materials
    - Troy Munro (MeEn)
    - David Allred (Physics)
  - Metallurgy
    - Tracy Nelson (Mfg En)
  - Reactor Design and Maintenance
    - Reactor Modeling
      - Matt Memmott (ChEn)
    - Manufacturing
      - Yuri Hovanski (Mfg En)
  - Salt Chemistry
    - Electrochemistry
      - John Harb (ChEn)
    - Modeling
      - Stella Nickerson (ChEn)

- Material behavior
- U and Th films
- Friction Stir Welding
- Molten salt reactor
- Manufacturing
- Corrosion
- DFT and MD
1. Convince that thermal conductivity is not easy to measure (and why)
2. Demonstrate past attempts to measure it for salts
3. Describe our devices and expected errors
4. Present current measurements
Why Thermal Conductivity ($k$) is Difficult to Measure
To measure the thermal conductivity, the following are needed:

1. A heat source
2. A temperature change
3. An accurate temperature sensor
4. Model relating temperature and heat transfer to property

\[
\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2}
\]

\[
q'' = -k \frac{dT}{dx}
\]
Background on Molten Halide Salt $k$ Measurements

- Previous methods:
  - parallel plates
  - coaxial cylinders
  - THW
  - laser flash
  - variable gap
  - optical scattering
  - freq. domain (TDTR, $3\omega$)

- Challenges:
  - electrical conduction
  - corrosion
  - convection, radiation
  - material compatibility

Magnusson, Memmott, Munro, Annals Nuc. Energy, 2020
https://doi.org/10.1016/j.anucene.2020.107608
Sensor Needs

To measure salt thermal conductivity, the device needs to account for:

1. Electrical isolation from salt
2. Corrosion resistance
3. High temperatures
4. How to reduce convection
5. How to account for radiation
6. Sample volume
7. Measurement time
8. Ensure thermal model matches experiment
How Have Halide Salts Been Measured?
Summary of pre-2000 measurements methods

- **Laser flash**
- **Variable Gap Apparatus**
- **Concentric Cylinders**
- **Forced Rayleigh Scattering**
Summary of unary salts up to 2018

Table 3. Data sets considered for the thermal conductivity of molten chloride salts at 0.1 MPa

<table>
<thead>
<tr>
<th>First author</th>
<th>Publication year</th>
<th>Purity (mass %)</th>
<th>Technique employed</th>
<th>Uncertainty quoted (%)</th>
<th>No. of data</th>
<th>Temperature range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>NaCl</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previous reference correlation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Janz¹</td>
<td>1979</td>
<td>...</td>
<td>(Based on Fedorov¹⁻)</td>
<td>20</td>
<td>...</td>
<td>1100–1200</td>
</tr>
<tr>
<td>Primary data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Golyshhev³</td>
<td>1992</td>
<td>...</td>
<td>Concentric cylinders (1 mm)</td>
<td>5.5</td>
<td>...</td>
<td>1075–1270</td>
</tr>
<tr>
<td>Harada⁴</td>
<td>1992</td>
<td>99.50</td>
<td>Laser flash (TD)</td>
<td>10</td>
<td>7</td>
<td>1086–1175</td>
</tr>
<tr>
<td>Nagasaka⁴</td>
<td>1992</td>
<td>99.00</td>
<td>Forced Rayleigh scattering (TD)</td>
<td>4</td>
<td>34</td>
<td>1170–1441</td>
</tr>
<tr>
<td>Veneraki⁸</td>
<td>1976</td>
<td>...</td>
<td>Concentric cylinders (1.37–2.19 mm)</td>
<td>8</td>
<td>...</td>
<td>1100–1216</td>
</tr>
<tr>
<td>Secondary data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smirnov⁵</td>
<td>1987</td>
<td>...</td>
<td>Concentric cylinders (1.2 mm)</td>
<td>4</td>
<td>6</td>
<td>1092–1150</td>
</tr>
<tr>
<td>Bystrai⁷</td>
<td>1975</td>
<td>...</td>
<td>Necked-down sample</td>
<td>10</td>
<td>16</td>
<td>1081–1186</td>
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<tr>
<td>Egorov⁸</td>
<td>1972</td>
<td>...</td>
<td>Concentric cylinders (2–3 mm)</td>
<td>10</td>
<td>7</td>
<td>1090–1230</td>
</tr>
<tr>
<td>Fedorov¹⁰</td>
<td>1970</td>
<td>...</td>
<td>Concentric cylinders (3 mm)</td>
<td>10</td>
<td>5</td>
<td>1101–1196</td>
</tr>
</tbody>
</table>

How do you know if you’re data is suspect?

Look at the slope of the data (it is expected to decrease)
Our Two Approaches

*Transient hot wire (THW) and Needle probe*
Overview

Needle Probe

• Modified THW combined with concentric cylinders method to limit convection
• Uses about 1 mL of salt
• Measurement time ~ 1 min
• Uncertainty ~ 5-10%

Diamond Encapsulated THW

• Based on a design used by groups with IUPAC and NIST for measuring liquids
• Uses about 1 mL of salt
• Measurement time ~ 1 sec
• Expected uncertainty 1-3%
  – Based on extensive error analysis and literature studies
Diamond Sensor
(Transient Hot Wire)

Still in development
Learning from measuring molten metals

Diamond Sensor Design

- Tungsten electrical pattern
- CVD diamond substrate and coating atop tungsten
- Multiple sensors produced
- Different ratios of “long” wire to “short” wire
Measurement Basis

- Hot-wire is both heater and thermometer
- Voltage change from balanced Wheatstone bridge relates to resistance change
- Resistance change provides temperature rise

*Connections D and E are used only for resistance measurements*
Sensor Holder + Crucible Prototype

Boron Nitride Sensor Holder (Two halves)

Boron Nitride Catch (Solid)

Nickel Crucible (Solid)
Experimental Data (Polymer Prototype)

Off due to unbalanced bridge
Property Determination

Potential Error Sources (FE model)

Based on analysis by Jarome Bilek (molten metals)

- Temperature stability of fluid ($\pm 2^\circ C$)
- Steady state resistances ($\pm 0.015\%$ Keithley 2000)
- Ratio between short and long wire resistances ($\approx \pm 0.03\%$)
- Length of hot wire (less than $\pm 0.2\%$)
- Temperature coefficient of resistance ($\pm 0.5\%$ for Pt)
  - Largest source of error
- Transient voltage from bridge circuit (less than $\pm 0.1\%$)
- Supply voltage ($\pm 0.005\%$)
- Radiation heat transport ($unknown$)

**Overall,** $\pm 1\%$ (we expect up to $\pm 3\%$)
1D Hot Wire Theoretical Corrections

- **Convection**
  - Short measurement times. Can be observed as deviation from linearity

- **Radiation**
  - Reduced with uniform surrounding temperature

\[
\delta T_R = \frac{8 \cdot \pi \cdot r_o \cdot \sigma \cdot T_o^3}{q} \cdot [\Delta T(r,T)]^2
\]

- **Finite wire properties**
  - \( \delta T_W(r,t) = \frac{q}{4 \cdot \pi \cdot \lambda} \left[ \frac{r_o^2 \left[(\rho \cdot C_p)_{W} - \rho \cdot C_p\right]}{2 \cdot \lambda \cdot t} \cdot \ln \left( \frac{4 \cdot \alpha \cdot t}{r_o^2 \cdot e^\gamma} \right) - \left( \frac{r_o^3}{2 \cdot \alpha \cdot t} \right) + \left( \frac{r_o^3}{4 \cdot \alpha_W \cdot t} \right) - \frac{\lambda}{2 \cdot \lambda_W} \right] \)

- **Finite wire diameter**

\[
\Delta T(r,t) = -\frac{q}{\pi^2 \cdot r_o \cdot \lambda} \int_0^\infty \left(1 - e^{-\alpha u^2 t}\right) \left\{ \frac{J_0(\alpha r) \cdot Y_1(\alpha r_o) - J_0(\alpha r_o) \cdot Y_1(\alpha r)}{u^2 \cdot \left[ J_1^2(w) - Y_1^2(w) \right]} \right\} \cdot du
\]

- **Variable fluid properties**
  - \( T_r = T_o + \frac{1}{2} \left[ \Delta T(t_1) + \Delta T(t_2) \right] \)

- **Outer boundary**

\[
\delta T_{OB}(r,t) = \frac{q}{4 \cdot \pi \cdot \lambda} \left\{ \ln \left( \frac{4 \cdot \alpha \cdot t}{b^2 \cdot e^\gamma} \right) + \sum_{v=1}^{\infty} e^{-\frac{g_v^2 \cdot \alpha t}{b^2}} \cdot \left[ \pi \cdot Y_v(g_v) \right]^2 \right\}
\]
Needle Probe

Currently used for measurements
Needle Probe (with HTTL at INL)
Analytical Model: Thermal Quadrupoles

\[
\begin{bmatrix}
\theta_0 \\
\phi_0
\end{bmatrix} = 
\begin{bmatrix}
A_1 & B_1 \\
C_1 & D_1
\end{bmatrix}
\begin{bmatrix}
1 & R_{c1\rightarrow 2} \\
0 & 1
\end{bmatrix}
\begin{bmatrix}
A_2 & B_2 \\
C_2 & D_2
\end{bmatrix}
\begin{bmatrix}
1 & R_{c2\rightarrow 3} \\
0 & 1
\end{bmatrix}
\begin{bmatrix}
A_3 & B_3 \\
C_3 & D_3
\end{bmatrix}
\begin{bmatrix}
1 & 0 \\
h\Gamma_{\text{crucible}} & 1
\end{bmatrix}
\begin{bmatrix}
\theta_4 \\
\phi_4
\end{bmatrix}
\]
Parametric Sensitivity Analysis

Water

Approximate Test Duration

Sodium Nitrate

Approximate Test Duration

Relative Change of $dT/dt$ (%) vs. Time (s)

- Power
- Cond. Probe
- Diff. Probe
- Rth Probe-Sample
- Cond. Sample
- Diff. Sample
- Sample Radius
- Rth Sample-Crucible
- Cond. Crucible
- Diff. Crucible
- Convection

Under Review
Model Fit and Monte Carlo Uncertainty

Water

- Experimental Data
- Fit Analytical Model
- Residuals

Temperature Rise (K)

Time (s)

Residuals (K)

Quantity

Thermal Conductivity [W/m·K]

Under Review
Results: $k < 0.20 \text{ [W/mK]}$

- Ethanol ($C_2H_5OH$)
  - RMSE: 0.048 W/mK (29.10%)
  - Uncertainty: 0.024 W/mK (11.03%)

- Propylene Glycol ($C_3H_8O_2$)
  - RMSE: 0.039 W/mK (19.59%)
  - Uncertainty: 0.034 W/mK (14.12%)

- Toluene ($C_7H_8$)
  - RMSE: 0.034 W/mK (26.00%)
  - Uncertainty: 0.017 W/mK (10.27%)

Under Review

radial to axial heat fluxes
Results: $0.40 < k < 0.66$ [W/mK]

**Water (H$_2$O)**
- RMSE: 0.026 W/mK (4.01%)
- Uncertainty: 0.034 W/mK (5.22%)

**Sodium Nitrate (NaNO$_3$)**
- RMSE: 0.046 W/mK (8.89%)
- Uncertainty: 0.033 W/mK (5.83%)

**Potassium Nitrate (KNO$_3$)**
- RMSE: 0.068 W/mK (16.5%)
- Uncertainty: 0.029 W/mK (6.06%)

Fresh SS316

Post-tests
Results: $k = 16.5$ [W/mK]

Galinstan (Ga-In-Sn)

RMSE: 6.17 W/mK (37.37%)
Uncertainty: 2.10 W/mK (19.11%)

Under Review
1. Validate probes in water (standard reference liquid)

2. Validate probes in nitrate salts ("low" temperature, reference correlations)

3. Measure in glovebox for fluoride salts, including FLiBe
   - FLiNaK planned before Thanksgiving

4. Work with INL to take additional measurements
Acknowledgements

Funding from the DOE DE-AC07-05ID14517, DE-NE0008870, NRC #31310019M0006

Diamond – Peter Kasper (project leader, MS student), Aaron Thorum (materials), Ara Bolander (COMSOL), Jon Dromey (sensor manufacturing), Crewse Petersen (holder manufacturing), Tom Carson (electrical), Conner Mantz (testing/analysis).

Needle Probe – Brian Merritt (project leader, MS student, NEUP fellow), Michael Seneca (testing and data processing), Spencer Larson (testing), Ben White (testing).

INL: Toni Y. Karlsson, David Tolman, Kurt Davis, Maria Del Rocio Rodriguez Laguna

Discussions: Marc Assael (Aristotle Univ.), Richard Perkins (NIST), Bill Wakeham (Imp. College London)

Contact: troy.munro@byu.edu
Extra Slides
Example of observing convection
Limited Data on Thermal Conductivity of Fluoride Salts

FLiNaK

FLiBe

FLiBe-ThF$_4$-UF$_4$

Magnusson, Memmott, Munro, Annals Nuc. Energy, 2020
Summary

<table>
<thead>
<tr>
<th>Table 1. Data sets considered for the thermal conductivity of molten nitrate salts at 0.1 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>First author</td>
</tr>
<tr>
<td>LiNO₃</td>
</tr>
<tr>
<td><strong>Previous reference correlation</strong></td>
</tr>
<tr>
<td>Janz⁷</td>
</tr>
<tr>
<td><strong>Primary data</strong></td>
</tr>
<tr>
<td>Asahina⁴⁶</td>
</tr>
<tr>
<td>Omotani⁷⁹</td>
</tr>
<tr>
<td><strong>Secondary data</strong></td>
</tr>
<tr>
<td>Araki³⁸</td>
</tr>
<tr>
<td>Tye³⁰</td>
</tr>
<tr>
<td>McDonald⁴⁷</td>
</tr>
<tr>
<td>Gustafsson⁴⁵</td>
</tr>
<tr>
<td>White⁴³</td>
</tr>
<tr>
<td>NaNO₃</td>
</tr>
<tr>
<td><strong>Previous reference correlation</strong></td>
</tr>
<tr>
<td>Nagasaka⁵⁰</td>
</tr>
<tr>
<td>Janz⁹¹</td>
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<tr>
<td><strong>Primary data</strong></td>
</tr>
<tr>
<td>Kitade⁴⁹</td>
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<tr>
<td>Asahina⁴⁶</td>
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<tr>
<td>Tufeu³⁰</td>
</tr>
<tr>
<td>Omotani⁷⁹</td>
</tr>
<tr>
<td>Odawara⁴⁴</td>
</tr>
<tr>
<td><strong>Secondary data</strong></td>
</tr>
<tr>
<td>Zhang⁴⁴</td>
</tr>
<tr>
<td>Obta⁷⁹</td>
</tr>
<tr>
<td>Santini⁷⁹</td>
</tr>
<tr>
<td>Kato³⁰</td>
</tr>
<tr>
<td>McDonald⁴⁷</td>
</tr>
<tr>
<td>Gustafsson⁴⁵</td>
</tr>
<tr>
<td>White⁴³</td>
</tr>
<tr>
<td>Bloom⁴³</td>
</tr>
</tbody>
</table>
Laser Flash

Thermal Conductivities of Molten Alkali Metal Halides

Makoto Harada, Akihisa Shioi,* Tsunetoshi Miura, and Shinsuke Okumi

Operation
- Laser pulse into sample (or crucible)
- Resulting temperature rise on opposite side measured
- $\alpha$ determined by time to have maximum intensity

Drawbacks
- Requires a 3-layer model to determine $\alpha$
- To determine $k$ from $\alpha$, also need $\rho$ and $c_p$
- Typical setups haven’t eliminated convection or parasitic heat losses
- Relative method
**Operation**

- Power is supplied to a thin, glass tube filled with mercury
- The resistance and temperature of the mercury is measured
- Termed “absolute method” requiring no calibration, and extensive theoretical background

**Drawbacks**

- Requires electrical isolation between “wire” and salt
- Temperatures limited by materials
**Variable Gap Apparatus** (variant of eat flow meter)

---

**Operation**
- Using heaters with known output and heat sinks, establish a temperature difference across a thin layer of the sample \( L \approx 500 \mu m \)
- Record the temperatures along the centerline above and below sample after reaching steady state
- Repeat at different thicknesses and analyzing using Fourier’s law, \( k = (\Delta L/\Delta T) \times q'' \)

**Drawbacks**
- Steady state can still result in convective heat losses
- Requires careful design to minimize radial heat losses
- Requires calibration since heat flux is hard to directly measure
Concentric Cylinders

Heat capacity and thermal conductivity of molten ternary lithium, sodium, potassium, and zirconium fluorides mixtures

V. Khokhlov *, I. Korzun, V. Dokutovich, E. Filatov

Journal of Nuclear Materials 410 (2011) 32–38

**Operation**
- Create gap between cylinders of low emissivity material
- Using heaters with known output and heat sinks, establish a temperature difference across a thin ring of the sample
- Record the temperatures across the gaps after reaching steady state
- Fit using $k = (\Delta L/\Delta T) \times q^\prime\prime$, and considers radiation

**Drawbacks**
- Steady state can still result in convective heat losses
- Difficult to ensure uniform gap
- Requires careful design to minimize axial heat losses
- Requires calibration since heat flux is hard to directly measure

![Diagram of the device](image.png)

Fig. 1. Device for measuring the thermal conductivity: 1, external cylinder; 2, internal cylinder; 3, heater; 4, thermocouples; 5, fixing screws; 6, thermal shields; 7, thermal screens; 8, cooled tube; 9, rubber stopper; 10, pipe for evacuation and supply of inert gas.
Forced Rayleigh Scattering

Measurement of the thermal diffusivity of liquids by the forced Rayleigh scattering method: Theory and experiment

Y. Nagasaka, a) T. Hatakeyama, M. Okuda, and A. Nagashima

**Operation**
- An interference pattern is created by splitting and then crossing modulated laser beams
- A probe beam is diffracted as a function of time
- $\alpha$ is determined from the spacing of the grating and change in intensity of the probe as a function of time

**Drawbacks**
- Highly dependent on absorption and transmission bands of the liquid
- To determine $k$ from $\alpha$, also need $\rho$ and $c_p$
- Sample size can impact the heat transfer model
Mass Diffusion Coefficient and Soret Coefficient of o-Dichlorobenzene Solutions of PCB and [60]Fullerene by the Soret Forced Rayleigh Scattering Method

Hiroaki Matsuura, Shintaro Iwaasa, and Yuji Nagasaka*
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Melting Temperature*</th>
<th>Density**</th>
<th>Dynamic Viscosity</th>
<th>Thermal Conductivity</th>
<th>Specific Heat Capacity, Isobaric</th>
<th>Electrical Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_m ) °C</td>
<td>( \rho ) g/cm(^3)</td>
<td>( \mu ) mPa-s</td>
<td>( k ) W/m-K</td>
<td>( c_p ) cal/g-K</td>
<td>( \sigma_e ) ( \Omega )^{-1}·cm^{-1}</td>
</tr>
<tr>
<td>LiF</td>
<td>848</td>
<td>1.63–1.82</td>
<td>1.38–2.21</td>
<td>1.20–2.22</td>
<td>0.58–0.60</td>
<td>8.16–10.41</td>
</tr>
<tr>
<td>LiF-BeF(_2)</td>
<td>458–459.1</td>
<td>1.82–2.03</td>
<td>1.86–13.91</td>
<td>1–1.19</td>
<td>0.56–0.58</td>
<td>1.34–2.51</td>
</tr>
<tr>
<td>LiF-NaF-KF</td>
<td>454–463.6</td>
<td>1.84–2.13</td>
<td>1.30–14.44</td>
<td>0.22–5.38</td>
<td>0.41–0.48</td>
<td>1.07–1.79</td>
</tr>
<tr>
<td>KF-ZrF(_4)</td>
<td>390–430</td>
<td>2.45–2.66</td>
<td>2.34–6.95</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NaF-KF-MgF(_2)</td>
<td>685–975</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>KCl-MgCl(_2)</td>
<td>423–440</td>
<td>1.46–1.69</td>
<td>2.44–6.01</td>
<td>0.54–0.63</td>
<td>0.24</td>
<td>0.59–0.74</td>
</tr>
<tr>
<td>LiF-BeF(_2)-ThF(_4)</td>
<td>356–485.8</td>
<td>2.64–3.66</td>
<td>7.06–16.53</td>
<td>–</td>
<td>0.32</td>
<td>1.38–2.61</td>
</tr>
<tr>
<td>LiF-BeF(_2)-UF(_4)</td>
<td>350–464</td>
<td>3.74–3.93</td>
<td>4.08–33.33</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LiF-BeF(_2)-ThF(_4)-UF(_4)</td>
<td>480–500</td>
<td>2.58–3.41</td>
<td>4.8–19.38</td>
<td>1.21–1.36</td>
<td>0.33–0.39</td>
<td>1.63–5.72</td>
</tr>
<tr>
<td>LiF-NaF-KF-ThF(_4)</td>
<td>450</td>
<td>1.8–2.2 (^{1})</td>
<td>1.95–9.20 (^{2})</td>
<td>–</td>
<td>0.45 (^{1})</td>
<td>–</td>
</tr>
<tr>
<td>LiF-NaF-KF-UF(_4)</td>
<td>452–560</td>
<td>1.8–2.5 (^{1})</td>
<td>1.7–9.0</td>
<td>4.0 (^{1})</td>
<td>0.40–0.44</td>
<td>–</td>
</tr>
</tbody>
</table>

* All property values presented here, excluding some melting temperature values and ranges marked with \(^{1}\), are the result of experimentation.

** All measured property values fall in the range of \( T_m\)–1000 °C with the exception of LiF (\( T_m\)=1300 °C).
Hot Wire Theoretical Corrections

- **Convection**
  - Short measurement times. Can be observed as deviation from linearity

- **Radiation**
  - Reduced with uniform surrounding temperature

\[ \delta T_R = \frac{8 \cdot \pi \cdot r_0 \cdot \sigma \cdot T_o^3}{q} \cdot [\Delta T(r,T)]^2 \]

- **Finite wire properties**
  - \[ \delta T_W(r,t) = \frac{q}{4 \cdot \pi \cdot \lambda} \cdot \left[ \frac{r_0^2 \left[ (\rho \cdot C_p)_W - \rho \cdot C_p \right]}{2 \cdot \lambda \cdot t} \cdot \ln \left( \frac{4 \cdot \alpha \cdot t}{r_0^2 \cdot e^\gamma} \right) - \frac{r_0^2}{2 \cdot \alpha \cdot t} + \frac{\lambda}{4 \cdot \alpha_W \cdot t} - \frac{\lambda}{2 \cdot \lambda_W} \right] \]

- **Finite wire diameter**
  - \[ \Delta T(r,t) = -\frac{q}{\pi^2 \cdot r_0 \cdot \lambda} \int_0^\infty \left( 1 - e^{-\alpha u^2 \cdot t} \right) \cdot \left\{ \frac{J_o(u r) \cdot Y_1(u r_o) - Y_o(u r) \cdot J_1(u r_o)}{u^2 \cdot [J_1^2(u r_o) - Y_1^2(u r_o)]} \right\} \cdot du \]

- **Variable fluid properties**
  - \[ T_r = T_o + \frac{1}{2} \cdot [\Delta T(t_1) + \Delta T(t_2)] \]

- **Outer boundary**
  - \[ \delta T_{OB}(r,t) = \frac{q}{4 \cdot \pi \cdot \lambda} \cdot \left\{ \ln \left( \frac{4 \cdot \alpha \cdot t}{b^2 \cdot e^\gamma} \right) + \sum_{v=1}^\infty \frac{e^{-\frac{e_r^2 \cdot \alpha \cdot t}{b^2}}}{b^2} \cdot \left[ \pi \cdot Y_v(g_v) \right]^2 \right\} \]
Hot Wire Method of Operation

\[
\delta T_1 = \frac{q}{4\pi\beta} \left[ r_0^2 \left( \frac{(\rho C_p)_w - \rho C_p}{2\beta t} \right) \ln \frac{4\alpha t}{r_0^2 e^t} - \frac{r_0^2}{2\alpha t} + \frac{r_0^2}{4\alpha_w t} \right]
\]

# Material Selection – Thermal Expansion

<table>
<thead>
<tr>
<th>Material</th>
<th>Linear Temperature Coefficient α (μm/m °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond (Carbon)</td>
<td>1.1 - 1.3</td>
</tr>
<tr>
<td>Invar</td>
<td>1.5</td>
</tr>
<tr>
<td>Graphite, pure (Carbon)</td>
<td>4-8</td>
</tr>
<tr>
<td>Tungsten</td>
<td>4.5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>5</td>
</tr>
<tr>
<td>Tantalum</td>
<td>6.5</td>
</tr>
<tr>
<td>Platinum</td>
<td>9</td>
</tr>
<tr>
<td>Nickel</td>
<td>13</td>
</tr>
<tr>
<td>Gold</td>
<td>14.2</td>
</tr>
<tr>
<td>Copper</td>
<td>16 - 16.7</td>
</tr>
<tr>
<td>Silver</td>
<td>19 - 19.7</td>
</tr>
<tr>
<td>Aluminum</td>
<td>21 - 24</td>
</tr>
</tbody>
</table>

Tungsten or Molybdenum
Density Measurements in Molten Chloride Salts by Neutron Attenuation and Comparison with Redlich-Kister Model

Molten Salt Thermal Properties Working Group, Virtual Workshop, University of South Carolina, November 15-17, 2021

Jisue Moon, Can Agca, Hunter Andrews, Jean-Christophe Bilheux, Alex Braatz, Abbey McAlister, Jake McMurray, Kevin Robb, Yuxuan Zhang, Joanna McFarlane
Interested in noble gas solubility in molten salts

• Solubility is the ratio of the volume of gas absorbed to the volume of absorbing liquid at temperature and pressure

• Henry’s law (limiting case – no chemistry)
  – The quantity of the gas dissolved is proportional to the pressure of the gas.
  – The concentration of the gas absorbed by the dissolving liquid is proportional to the pressure (concentration in the gas phase) giving the temperature dependent Henry’s law constant (K)

• An Arrhenius plot will give the enthalpy of solution
  – \[ \ln K = -\Delta H_{\text{sol}} / RT \]
Densities in salt systems of interest for solubility measurements

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Salt Mixtures</th>
<th>Composition (mole fraction)</th>
<th>Composition (mass fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>eutectic NaCl/KCl</td>
<td>NaCl - 50</td>
<td>KCl - 50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaCl - 0.44</td>
</tr>
<tr>
<td>2</td>
<td>UCl₃ – KCl mixture 1 *</td>
<td>KCl - 43</td>
<td>UCl₃ - 57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>KCl - 0.14</td>
</tr>
<tr>
<td>3</td>
<td>UCl₃ – KCl mixture 2 *</td>
<td>KCl - 78</td>
<td>UCl₃ - 22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>KCl - 0.43</td>
</tr>
<tr>
<td>5</td>
<td>eutectic KCl-UCl₂-NaCl *</td>
<td>NaCl - 22</td>
<td>KCl - 52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaCl - 0.09</td>
</tr>
<tr>
<td>6</td>
<td>KCl-MgCl₂ eutectic 1 #</td>
<td>KCl - 42</td>
<td>MgCl₂ - 58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>KCl - 0.36</td>
</tr>
<tr>
<td>7</td>
<td>solar - NaCl/KCl/MgCl₂</td>
<td>NaCl - 21</td>
<td>KCl - 49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgCl₂ - 30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaCl - 0.16</td>
</tr>
<tr>
<td>8</td>
<td>KCl-MgCl₂ eutectic 2 #</td>
<td>KCl - 63</td>
<td>MgCl₂ - 37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>KCl - 0.57</td>
</tr>
<tr>
<td>9</td>
<td>ZrCl₄-KCl</td>
<td>ZrCl₄ - 28</td>
<td>KCl - 72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ZrCl₄ - 0.55</td>
</tr>
</tbody>
</table>

- Sample was pre-mixed, loaded into 5mm quartz NMR tube and sealed
- Each quartz tube was loaded into a stainless-steel liner

# Janz, J Phys Chem Ref Data, 4, 871 (1975)
Sample loading

- Density measurements using neutron imaging were performed on CG-1D at the High-Flux isotope reactor (HFIR), Oak Ridge National Laboratory (ORNL)
- Sample holder was attached to a stick that will go into the furnace
- After loading the stick into the furnace, the system was evacuated before heating
- Conduct three separate experiments with different samples as follow:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Tube location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp1(0-1-7-9)</td>
<td>Empty</td>
</tr>
<tr>
<td>Exp2(2-1-3-5)</td>
<td>UCl₃ - KCl mixture 1</td>
</tr>
<tr>
<td>Exp3(6-1-8-9)</td>
<td>eutectic 1 KCl-MgCl₂</td>
</tr>
</tbody>
</table>
## Experiment heating programmed step

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Tube location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp1(0-1-7-9)</td>
<td>Empty</td>
</tr>
<tr>
<td></td>
<td>eutectic NaCl/KCl</td>
</tr>
<tr>
<td></td>
<td>solar - NaCl/KCl/MgCl₂</td>
</tr>
<tr>
<td></td>
<td>ZrCl₄-KCl</td>
</tr>
<tr>
<td>Exp2(2-1-3-5)</td>
<td>UCl₃ – KCl mixture 1</td>
</tr>
<tr>
<td></td>
<td>eutectic NaCl/KCl</td>
</tr>
<tr>
<td></td>
<td>UCl₃ – KCl mixture 2</td>
</tr>
<tr>
<td></td>
<td>eutectic KCl-UCl₃-NaCl</td>
</tr>
<tr>
<td>Exp3(6-1-8-9)</td>
<td>Eutectic 1 KCl-MgCl₂</td>
</tr>
<tr>
<td></td>
<td>eutectic NaCl/KCl</td>
</tr>
<tr>
<td></td>
<td>Eutectic 2 KCl-MgCl₂</td>
</tr>
<tr>
<td></td>
<td>ZrCl₄-KCl</td>
</tr>
</tbody>
</table>

### Experiment 1

1. Test ramping to 450°C and cooled to RT
2. Step heating from 400°C to 800°C at 5°C/min and hold at each 25°C increment for 30 min
3. Cool to RT

### Experiment 2

1. Initial heating to 800°C with 5°C/min
2. Cool to 400°C
3. Step heating from 400°C to 800°C with 5°C/min. Hold at each 25°C increment for 30 min
4. Cool to 400°C
5. Step heating to 800°C (same as step 3)
6. Cool to RT

### Experiment 3

1. Pre-heating to 800°C
2. Cool to 400°C
3. Step heating from 400°C to 800°C at 5°C/min. Hold at each 25°C increment for 30 min
4. Cool to 400°C
5. Step heating from 400 to 800°C at 5°C/min. Hold at each 25°C increment for 30 min
6. Step cooling
Density measurement from neutron imaging

- Obtaining diameter information from each top of the tube (empty space at the temperature)
- Obtaining height information from the salt height
  - Height was divided into two areas;
  - height 1) without curvature 2) with curvature
- Use the volume of the cylinder and consider the bottom volume that is caused by spherical bottom
- Measured the tube diameter using the unfilled area at the top because the salt-quartz interface is not clear
X-axis profile analysis

• x-axis profile shows that salt does not have uniform density
Profile analysis for UCl₃ mixtures at 800°C

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Tube location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp2(2-1-3-5)</td>
<td>UCl₃ – KCl mixture 1</td>
</tr>
<tr>
<td></td>
<td>eutectic NaCl/KCl</td>
</tr>
<tr>
<td></td>
<td>UCl₃ – KCl mixture 2</td>
</tr>
<tr>
<td></td>
<td>eutectic KCl-UCl₃-NaCl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>Sample#</th>
<th>Temperature (°C)</th>
<th>Volume(cm³)</th>
<th>Mass(g)</th>
<th>Measured Density(g/cm³)</th>
<th>Theoretical Calculated Density(g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP2-#1</td>
<td>UCl₃ – KCl mixture 1</td>
<td>2</td>
<td>800</td>
<td>0.200</td>
<td>0.6069</td>
<td>2.939</td>
<td>3.035</td>
</tr>
<tr>
<td>EXP2-#3</td>
<td>UCl₃ – KCl mixture 2</td>
<td>3</td>
<td>800</td>
<td>0.427</td>
<td>0.9394</td>
<td>2.198</td>
<td>2.341</td>
</tr>
<tr>
<td>EXP2-#4</td>
<td>eutectic KCl-UCl₃-NaCl</td>
<td>5</td>
<td>800</td>
<td>0.488</td>
<td>0.8795</td>
<td>1.802</td>
<td>1.903</td>
</tr>
</tbody>
</table>
The degree of expansion is not much compared to higher concentration of UCl₃

There is height expansion as temperature increased to 800°C

Volume expansion?
Profile distribution of UCl₃ - KCl mixture 1

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>Volume /cm³</th>
<th>Volume Change /cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.184</td>
<td>0.000</td>
</tr>
<tr>
<td>450</td>
<td>0.196</td>
<td>0.012</td>
</tr>
<tr>
<td>500</td>
<td>0.209</td>
<td>0.025</td>
</tr>
<tr>
<td>550</td>
<td>0.215</td>
<td>0.031</td>
</tr>
<tr>
<td>600</td>
<td>0.217</td>
<td>0.033</td>
</tr>
<tr>
<td>650</td>
<td>0.221</td>
<td>0.037</td>
</tr>
<tr>
<td>700</td>
<td>0.226</td>
<td>0.043</td>
</tr>
<tr>
<td>750</td>
<td>0.232</td>
<td>0.048</td>
</tr>
<tr>
<td>800</td>
<td>0.237</td>
<td>0.053</td>
</tr>
</tbody>
</table>

Profile distribution of UCl₃ – KCl mixture 2

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>Volume /cm³</th>
<th>Volume Change /cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.378</td>
<td>0.000</td>
</tr>
<tr>
<td>450</td>
<td>0.379</td>
<td>0.001</td>
</tr>
<tr>
<td>500</td>
<td>0.380</td>
<td>0.002</td>
</tr>
<tr>
<td>550</td>
<td>0.395</td>
<td>0.017</td>
</tr>
<tr>
<td>600</td>
<td>0.403</td>
<td>0.025</td>
</tr>
<tr>
<td>650</td>
<td>0.411</td>
<td>0.033</td>
</tr>
<tr>
<td>700</td>
<td>0.421</td>
<td>0.043</td>
</tr>
<tr>
<td>750</td>
<td>0.430</td>
<td>0.052</td>
</tr>
<tr>
<td>800</td>
<td>0.440</td>
<td>0.062</td>
</tr>
</tbody>
</table>
Eutectic KCl-UCl$_3$-NaCl

Not uniform until 750°C-void?

<table>
<thead>
<tr>
<th>Temp. /°C</th>
<th>Volume /cm$^3$</th>
<th>Volume Change /cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.476</td>
<td>0.000</td>
</tr>
<tr>
<td>450</td>
<td>0.476</td>
<td>0.000</td>
</tr>
<tr>
<td>500</td>
<td>0.476</td>
<td>0.000</td>
</tr>
<tr>
<td>550</td>
<td>0.479</td>
<td>0.003</td>
</tr>
<tr>
<td>600</td>
<td>0.483</td>
<td>0.007</td>
</tr>
<tr>
<td>650</td>
<td>0.483</td>
<td>0.007</td>
</tr>
<tr>
<td>700</td>
<td>0.499</td>
<td>0.023</td>
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<tr>
<td>750</td>
<td>0.494</td>
<td>0.018</td>
</tr>
<tr>
<td>800</td>
<td>0.503</td>
<td>0.027</td>
</tr>
</tbody>
</table>
Volume change comparison

- Volume change after melting at 500°C, slope = 0.0002 cm³/K for UCl₃-KCl mixture 2 (teal)

- Volume change after melting at 550°C, slope = 9x10⁻⁵ cm³/K, for UCl₃-KCl mixture 1 (green)

- Volume change after melting at 750°C, slope = 0.0002 cm³/K, for UCl₃-KCl-NaCl (dark blue) See bubble captured in the salt (up to 700°C)
### Profile analysis for MgCl₂, ZrCl₄, KCl mixtures at 800°C

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample #1</th>
<th>Sample #2</th>
<th>Sample #3</th>
<th>Sample #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp3(6-1-8-9)</td>
<td>Eutectic 1 KCl-MgCl₂</td>
<td>eutectic NaCl/KCl</td>
<td>Eutectic 1 KCl-MgCl₂</td>
<td>ZrCl₄-KCl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Volume (cm³)</th>
<th>Mass (g)</th>
<th>Measured Density (g/cm³)</th>
<th>Theoretical Calculated Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXP3-#1</td>
<td>eutectic 1 KCl(42)-MgCl₂(58)</td>
<td>6</td>
<td>800</td>
<td>0.328</td>
<td>0.5476</td>
<td>1.571</td>
</tr>
<tr>
<td>EXP3-#2</td>
<td>eutectic NaCl(50)/KCl(50)</td>
<td>1</td>
<td>800</td>
<td>0.555</td>
<td>0.8638</td>
<td>1.497</td>
</tr>
<tr>
<td>EXP3-#3</td>
<td>Eutectic 2 KCl(63)-MgCl₂(37)</td>
<td>8</td>
<td>800</td>
<td>0.409</td>
<td>0.6423</td>
<td>1.519</td>
</tr>
<tr>
<td>EXP3-#4</td>
<td>ZrCl₄(28)-KCl(72)</td>
<td>9</td>
<td>800</td>
<td>0.479</td>
<td>0.8770</td>
<td>1.832</td>
</tr>
</tbody>
</table>
Profile comparison (exp3)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube location</td>
<td>Eutectic 1 KCl-MgCl₂</td>
<td>eutectic NaCl/KCl</td>
<td>Eutectic 2 KCl-MgCl₂</td>
<td>ZrCl₄-KCl</td>
</tr>
<tr>
<td>Exp3(6-1-8-9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>475 °C</td>
<td>685 °C</td>
<td>425 °C</td>
<td>525 °C</td>
</tr>
</tbody>
</table>

≥ 500 °C
≥ 700 °C
≥ 450 °C
≥ 600 °C
Volume change with temperature

### Table

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1.eutectic KCl(42)-MgCl2(58)</th>
<th>2.eutectic NaCl-KCl</th>
<th>3.eutectic KCl(63)-MgCl2(37)</th>
<th>4.ZrCl4(28)-KCl(72)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>450</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0174</td>
<td>0.0000</td>
</tr>
<tr>
<td>500</td>
<td>0.0317</td>
<td>0.0000</td>
<td>0.0225</td>
<td>0.0000</td>
</tr>
<tr>
<td>550</td>
<td>0.0409</td>
<td>0.0000</td>
<td>0.0276</td>
<td>0.0000</td>
</tr>
<tr>
<td>600</td>
<td>0.0448</td>
<td>0.0000</td>
<td>0.0301</td>
<td>0.0026</td>
</tr>
<tr>
<td>650</td>
<td>0.0461</td>
<td>0.0000</td>
<td>0.0352</td>
<td>0.0227</td>
</tr>
<tr>
<td>700</td>
<td>0.0500</td>
<td>0.0058</td>
<td>0.0378</td>
<td>0.0315</td>
</tr>
<tr>
<td>750</td>
<td>0.0526</td>
<td>0.0207</td>
<td>0.0429</td>
<td>0.0410</td>
</tr>
<tr>
<td>800</td>
<td>0.0571</td>
<td>0.0343</td>
<td>0.0479</td>
<td>0.0531</td>
</tr>
</tbody>
</table>

7E-5 cm³/K after melting point
2E-4 cm³/K after melting point
8E-5 cm³/K after melting point
3E-4 cm³/K after melting point
Work in progress

• Measuring xenon solubilities in chloride salts
• Will use densities to get molar concentrations and heats of solution
Conclusions

• Imaging allows us to view the salt as it expands and contracts through the phase transition

• Voids and bubbles are present that sometimes only dissipate after several cycles

• Cooling curves provide lower uncertainties than heating curves because of the entrained voids

• Thermophysical measurements require extended equilibration times (thermal/solubility/etc) to reduce the effect of interfacial properties
Funding & Reference

• Funding was provided by the US Department of Energy ARPA-E Meitner project in collaboration with Moltex Energy, the US Department of Energy Nuclear Energy Advanced Modeling and Simulation Program and The Advanced Reactor Technologies Molten Salt Reactor Campaign.

• The neutron radiography used resources at the HFIR, a DOE Office of Science User Facility operated by ORNL

Remote Density Measurements of Molten Salts using Neutron Radiography

Alexander Long (MST-8), Scott Parker (MST-16), Marisa Monreal (C-IIAC), J. Matt Jackson (MST-DO), D. Travis Carver (MST-8), and Sven Vogel (MST-8)

November 16th 2021

Molten Salt Thermal Properties Working Group, Virtual Workshop
Using Neutron Radiography to Measure Density

Neutron radiography can be used to measure heights (2D) and volumes (3D) of well-known quantities of salts at relative temperatures to determine densities.

Developing measurements with neutron radiography adds an additional technique to compare to already established methods and opens up the ability to measure otherwise difficult samples.

Some Advantages...

- You have eyes on the sample the whole time (watch out for bubbles!).
- Can have compact design that allows for less sample materials.
- Modular setup: samples can be swapped quickly. Measurement times depend mostly on furnace.
- Can measure same samples multiple times.
- Suitable hazardous materials (PuCl₃).
- Potential to extract a lot of additional information with more advanced neutron imaging techniques. Temps and actinide density can be measured in-situ with neutron resonances.

3. Williams et. al. “Application and testing of a triple bubbler sensor in molten salts” Nuclear Engineering and Technology (2020)
The Los Alamos Neutron Science Center (LANSCE)
Neutron Radiography Setup On FP5 for Molten Salts

Information on setup

**Camera:** Atik 490ex (CCD: 3.69 µm²/pixel)

**Scintillator Screen:** GdO₂S:Li or ZnS:Li

**Resolution @ Scintillator:** ~30-50 µm²/pixel

**Furnace:** Carbolite-Gero Tube Furnace

**Max Temps:** ~1150 °C

**Neutron Energies:** Thermal to Epi-Thermal

**Sample Containers:** 0.25” Swagelok tubing

**Containment Materials:** 304 Stainless Steel

- Calibration ruler with well known geometry.
- Linear motion stage to lift complete furnace setup.
- Multiple exposures to cover height of samples.
- Measured multiple well know salt mixtures.
- Two samples could be measured in ~12 hours.
- Images were averaged over 3 five min exposures
Measuring Heights of Fluids and Determining Volumes

- Images ratios at different temperatures were used to isolate changes in meniscus heights.

- Line profiles over meniscus were fitted with an error functions.

\[ G(y) = A \ erf \left( \frac{y - y_0}{\sqrt{2}\sigma} \right) \]

- \( y_0 \): centroid of normal distribution
- \( \sigma \): the standard deviation

- CTE for 304 stainless steel was measured and used to adjust volumes at any given temperature.
- Assuming radial symmetry of ¼” Swagelok tubing, volumes were determined for three different regions.
- Volume of bottom cap was determined separately.
- With masses measured before hand, densities could be determined at each temperature.
Density Results

After measuring well known salt samples, various single- and multi-component liquid chlorides were examined.

**Single Comp:** NaCl, LiCl, KCl, CaCl$_2$, and MgCl$_2$

**Binary** LiCl + KCl, MgCl$_2$+NaCl, NaCl+KCl, MgCl$_2$+KCl,

**Eutectics:** NaCl+UCl$_3$, and KCl+UCl$_3$

**Ternaries:** NaCl + KCl + UCl$_3$ and LiCl +KCl + UCl$_3$

In addition, the NaCl + UCl$_3$ system was examined with varying molar concentrations of depleted uranium.

Thermophysical Properties of Liquid Chlorides from 600 – 1600K. *J. Molecular Liquids* (accepted!)
Looking Forward…

Part of NE-GAIN with TerraPower to measure PuCl$_3$-based salts using neutron radiography at LANSCE.

Building a custom compact tube furnace…
- Improved overall accuracy with better imaging geometry.
- Allow for sample rotation for nCT of meniscus shape.
- House high hazardous samples with multiple levels of containment.

*Parts have been ordered and tests will be soon underway!*

- Additional density measurements are planned for December 2021 with both U and non-U based mixtures.
- Exploring viscosity measurements with neutron radiography (using compact furnace)
- Have plans to perform Energy Resolved Neutron Imaging measurements on salts to map out actinide distributions at temperatures.
Thank you for this opportunity and your time!

LANSCE 2022 Run Cycle:
June 2022 – December 2022
Accepting proposals for PAC March 2022

Density measurements on FP5 at LANSCE


Funding: LANL LDRD Office (20210113DR & 20190650DI)