Brownian Motion and Viscosity

Well-established methods of measuring viscosity in molten salts require the creation of well-defined fluid flow. An alternative “flow-free” method that we are developing utilizes Brownian motion of microspheres, whose mean square displacements (MSD) are related to the liquid’s viscosity via the Stokes-Einstein relationship:

\[ \langle \Delta x^2 \rangle = 2Dt, \quad D = \frac{k_BT}{6\pi \eta r}, \quad \therefore \eta = \frac{k_BTt}{3\pi r \langle \Delta x^2 \rangle} \]

Calculating Mean Square Displacement

The MSD is calculated by acquiring a microsphere’s motion using an optical microscope and camera. A gaussian is fit to the particle scattering intensity which then determines its position. The particle displacement evaluated at different relative times is taken for all images (58 fps for 1000 frames). The individual displacements in both the \( x \) and \( y \) directions are binned together into a histogram. A gaussian is then fit to the displacement histogram, where the fitted variance is equivalent to the MSD. MSD is plotted against the relative time and fit to a line. This linear fit is the diffusion coefficient, and thus can be compared to the Stokes-Einstein relationship.

Solution and Sample Cell

A powder of monodisperse silica microspheres 1.7 \( \mu m \) in diameter was stirred into a beaker of water and sonicated. A sample cell was created by placing a microscope slide on top of a concave depression in a graphite block. The solution is injected into the cell via a syringe passed into a channel carved from the edge of the block to the depression. After injection, the channel is sealed shut to prevent exposure to air, and thus prevent fluid flow via evaporation.

Results

First frame

Last Frame

Particle’s path traveled

Histogram of \( x-y \) displacement

MSD, \( D \), and \( \eta \) values averaged over 11 runs

Future Work: Molten Salts

(right) Furnace where molten salt samples will be tested. (above) Crucible in which salt samples will be contained

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 \( z \)
2. The particle radius
3. \( \sim 5x \) faster frame rates

References

Molten Fluoride Optical Spectroscopy
Will Derdeyn¹, Sara Mastromarino², Mark Anderson¹, Raluca Scarlat²
Department of Engineering Physics, UW-Madison¹
Department of Nuclear Engineering, UC-Berkeley²

MOTIVATION
Molten fluoride optical (visible/NIR, NIR/MIR/FIR) spectroscopy has several applications:
- Deduction of changes in coordination environment (e.g. CN, oxidation state)
- Measurement of thermochemical properties and reaction kinetics
- Detection of chemical species
- Data for radiative heat transfer

LITERATURE METHODS
Transmittance methods
Demonstrated material combinations:
- Graphite body with unsealed diamond windows (Fig. 1) [1]
- Hastelloy body with graphite-sealed diamond/SiC windows
- Ni body w/ Au liner and Au-sealed diamond window
Best for visible/NIR region
- Simpler optics
- Straightforward path length measurement

LITERATURE DATA
Electronic
3d and 4f absorption results in peaks throughout visible/NIR. U⁴⁺ in FLiBe [3] shown in Fig. 3.
Ni²⁺, Cr³⁺, Fe³⁺, Fe⁵⁺, Co²⁺, Mn²⁺, Mn³⁺, Cu²⁺, Nb⁴⁺, Ta⁵⁺, Ce³⁺, Pr³⁺, Gd³⁺, Pa⁴⁺, U³⁺, Pu⁴⁺
Various solvents: FLiNaK, FLiBe, LiF-BeF₂-ThF₄, CaF₂, BeF₂, LiF-NaF, NaF, LiF, KF, CsF

LITERATURE APPLICATIONS
Study of UF₃ oxidation by graphite [6]
In MSR, UF₃/UF₄ equilibrium was controlled by Be reduction to give small concentration of UF₃. There was some concern about reaction of UF₃ with graphite to form UC₂.

\[3UF₃ + UC₂ \rightarrow 4UF₄ + 2C\]

Equilibrium shifts from left to right with increasing temperatures (Fig. 5) and increasing fluoroacidity
- Heat of solutions for UF₃ and UF₄ estimated using Van Hoff’s equation

Corrosive attack of Cr by CrF₃ [7]
Potential for corrosion via the following reaction:
\[2CrF₃ + Cr \leftrightarrow 3CrF₂\]
Right side heavily favored in FLiBe (Fig. 6, left)
Left side heavily favored in FLiNaK (Fig. 6, right)
Increasing fluoroacidity favors lower valency.
Higher valence ions prefer higher CN (predicted by AIMD [8]).

EXPERIMENTAL PLANS
A useful engineering application for visible/NIR measurements is the detection of corrosion products in molten fluorides. The has been demonstrated for fission products in molten chlorides [9], but not yet for molten fluorides.
- Benchmarking with controlled additions of CrF₃, FeF₂, and NiF₃ to FLiBe followed by tests of samples from natural convection loop [10].
- Preliminary testing with nitrates and chlorides outside of glovebox is underway.

ACKNOWLEDGEMENTS
This research has been performed using funding received from the DOE Office of Nuclear Energy’s Nuclear Energy University Programs DE-NE0008680 (Project 17-13232). This work has also been supported through the US Nuclear Regulatory Commission Graduate Student Fellowship program on Grant NRC-HQ-84-15-G-0040. Seth Jones is gratefully acknowledged for assistance with design and fabrication.

REFERENCES
References


Acknowledgements

This research was undertaken, in part, thanks to funding from the Canada Research Chairs program (850-2031328) of the Natural Sciences and Engineering Research Council of Canada. The NSERC Discovery Grants program is greatly acknowledged for partial funding of these projects. The Canadian Foundation for Innovation is gratefully acknowledged for funding the purchase of the Simultaneous Thermal Analyzer. Much appreciation to E. Capelli, J.A. Ocádiz-Flores, O. Beneš, D. Hallatt, and K. Lipkina for useful discussions.

Fluorination

HF can be used for fluorination of ThO₂, UO₃, PuO₂, or purification of fluorides with these oxides present. We wish to avoid the direct use of HF as it is hazardous to store and use. Rather than using fluorinating agents directly, we can use ammonium bifluoride (NH₄HF₂).

- Fluorination of ThF₄ with NH₄HF₂ has been successful and reported in the open literature: E. Capelli [1] and M. Beilmann [2].
- In both cases, Differential Scanning Calorimetry (DSC) was in agreement with the reference melting point (1110±3 °C [3]).
- Ocádiz-Flores followed Capelli’s approach but was unable to obtain pure ThF₄. XRD reported the formation of (NH₄)₂ThF₃.

Approaches to purification and dehydration stage by other authors.

Results

Earlier batches of ThF₄ showed a strong darkening during purification in the Ni crucible; a melting peak with a shoulder is observed on DSC but is not repeatable. The ThF₄ was not successfully purified.

Later work using a glassy carbon crucible showed only a very mild darkening during purification; the specimen is awaiting XRD and DSC temperature analysis.

Methodology

<table>
<thead>
<tr>
<th>Purification Stage</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄HF₂</td>
<td>250</td>
<td>12</td>
<td>Sealed reaction vessel</td>
</tr>
<tr>
<td>ThF₄</td>
<td>400</td>
<td>6</td>
<td>Open Ni vessel</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dehydration Stage</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄HF₂</td>
<td>430</td>
<td>3</td>
<td>Open Ni vessel</td>
</tr>
<tr>
<td>ThF₄</td>
<td>450</td>
<td></td>
<td>to glovebox</td>
</tr>
</tbody>
</table>

Table 1. Approaches to purification and dehydration stage by other authors.

After our group reviewed the literature and having multiple discussions with Capelli (Delft University of Technology), Beneš (JRC, Karlsruhe), and Ocádiz-Flores (Delft), all of whom used a similar process, it is clear that this process is not very robust or reproducible.

Conclusions

Using the ammonium bifluoride method with a glassy carbon crucible to hold the NH₄HF₂ and ThF₄ layers during all heating operations has lightened the final colour of the fuel salt, which is an indicator of purity. This salt has yet to undergo DSC, which will be a more conclusive test of purity.

Fluorination of ThF₄ Using the Ammonium Bifluoride Method

ThF₄ in glassy carbon crucible is awaiting DSC

Figure 1. Milling ThF₄

Figure 2. Dehydration

Figure 3. Nickel pressure vessel for fluorination.

Figure 4. Differential Scanning Calorimetry and X-ray diffraction spectroscopy of “darker” specimen

Figure 5. Comparison of photographs of “lighter” specimen in glassy carbon crucible to hold the NH₄HF₂ and ThF₄ layers during all heating operations.

ThF₄ in glassy carbon crucible is awaiting DSC
Coupling Gibbs Energy Minimisation & Phase Field for Corrosion Modelling in Molten Salt Reactors

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https://nuclear.ontariotechu.ca/pino

Acknowledgements

This work was supported by the Department of Energy Nuclear Science Advanced and Simulation program.

The analyses were done as part of the High-Power Computing Center at Idaho National Laboratory, which is supported by the US Office of Nuclear Energy of the Department of Energy and in collaboration with the Nuclear Science User Facilities. This research was undertaken, in part, thanks to funding from the Canada Research Chairs (950-231328) program of the Natural Sciences and Engineering Research Council of Canada. This research made use of the resources of the High-Performance Computing Center at Idaho National Laboratory, which is supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities. This work was funded by the Department of Energy Nuclear Energy Advanced Modeling and Simulation program.

Demonstration Problem A – Cahn-Hilliard

Initial Conditions

Chemical Potential

Temperature Distribution

Chemical Potential – KF

Chemical Potential – NiF₂

Gem Field Phase Coupling

Phase-field solver provides the system composition, temperature and pressure as inputs at each node and/or

• Provides quantities such as Gibbs energy, chemical potentials, susceptibilities, etc.

• Gibbs Energy Minimizer supports phases modelled using the Modified Quasichemical Model in Quadruplet Approximation (MQMQA), Compound Energy Formalism (CEF), ideal solution model and regular substitutional approximation (RSA) to calculate microstructural evolution.

• Gibbs energy minimisation supports phase-field models using the Modified Quasichemical Model in Quadruplet Approximation (MQMQA), Compound Energy Formalism (CEF), ideal solution model and regular substitutional approximation (RSA) to calculate microstructural evolution.

Demonstration Problem B – Phase Field Coupling

Final Ni Distribution (Time: 100.0 s)

Chemical Potential Induced Nickel Diffusion

Initial Ni Distribution (Time: 0.0 s)

Conclusions

• Predicting the corrosion rate of alloys in contact with molten salt can hasten the development of Molten Salt Reactors but no capability exists to model the influence of corrosion on the behaviour of structural materials.

• Yellowjacket is aimed at developing corrosion modelling capability for Molten Salt Reactors.

• Yellowjacket couples GEM with the Phase Field method to predict corrosion at mesoscopic scale and allows integrating continuum mechanics codes with those representing chemical phenomena.

REFERENCES


**Ab initio** simulation of the LiCl-KCl system


**Motivation**
With the goal of removing carbon from the power sector and then the whole economy there is a need for generation IV reactors. There exists a knowledge gap in the thermophysical properties of molten salts at the operational temperatures for the molten salt reactors.

**System Equilibration**
Ab initio molecular dynamics simulations have been performed on eleven distinct LiCl-KCl systems with a temperature range from 700 to 1300 K following the contour of the phase diagram. The simulations were executed with the Vienna Ab initio Simulation Package with 200 atoms. To adjust for dispersion forces, the vdw-DF2 van der Waals function was applied in the NVT ensemble with a Langevin thermostat. First, the systems were melted and mixed at 2000 K for 15 ps. Following this, the systems were quenched to their respective temperatures and then allowed to equilibrate for 10 ps. To find the equilibrium volume the volume was perturbed to create pressure as a function of volume. The equilibrium volume is then found by fitting a parabolic function. For statistics, each curve consists of five unique volumes, each containing five simulations for 5 ps, and the pressure was averaged over the last 4 ps. For uniformity for the bulk modulus, the pressure range fitted was 7 to -2 kBar.

**Dispersion correction**
Within ionic liquids, van der Waals (vdW) forces play an important role in the structure and properties. The most common density functionals do not correctly describe the vdW interaction between molecules. This study performed a down-selection of seven unique dispersion interactions. The selected option was the vdw-DF2 function because it followed the general trend observed in the density. This was not the minimum error, but the method best suited for the full compositional spectrum.

**Experimental Setup**
The experimental densities were measured using the direct Archimedean method. A Ni 200 alloy bobber was used with dimensions of 12.8 in diameter and 20 mm in height. A tungsten wire was used along with a glassy carbon crucible. A Mettler-Toledo WXTS204 balance was used for measurement with a 0.1 mg precision. error in the thermometer ranged from 2.5 to 3.5 K.

**Density**
The figures below show the influence of temperature and composition on the density of LiCl-KCl. The simulations match the experimental densities better closer to the eutectic composition. Overall there is good agreement with experiments.

**Compressibility**
The trend observed in LiCl-KCl is that as the concentration of KCl increases so does the compressibility and likewise, as the temperature increase so does the compressibility.

**Gibbs free energy of mixing**
Gibbs free energy of mixing can be calculated from the enthalpy of mixing and with the ideal solution model the entropy term can be added. The observable trends are that as the temperature increases the Gibbs free energy decreases. There is good agreement with the literature.

**Heat capacity**
The two trends in the isobaric heat capacity that can be observed are that as temperature increases the heat capacity decreases and as LiCl-KCl becomes more KCl rich the heat capacity increases. Values are within 8.8% of the literature.

**Summary**
This study showed that AIMD can be used can calculate the density of molten salts accurately compared to historical studies and new measurements. This study presented which dispersion correction can be used for the full spectrum of LiCl-KCl. The compressibility, isobaric heat capacity, and Gibbs energy of mixing were calculated and compared to literature when available.

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G.J. Janz, American Chemical Society and the American Institute of Physics, 1988.
URL https://www.crct.polymtl.ca/fact/documentation/FTsalt/FTsalt_Figs.htm
Implementation of an Experimental Setup Based on the Three-Omega Method for Thermal Conductivity Measurements of Molten Salts

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E-mail: rocio.rodriguez@inl.gov

GOALS

Main goal
Produce high-fidelity thermal conductivity data on molten material/salts at high temperature

Sub-goals
- Design and fabricate a three-omega sensor
- Assemble an electric circuit capable of accurately measuring the three-omega (3ω) voltage.
- Develop a reliable thermal model to link the experimental measurement to the thermal conductivity.

MOTIVATION

To design, model, predict, license, and operate molten salt reactors (MSRs), the behavior of the fuel and coolant must be understood as a function of temperature. Of particular importance is the reliable and reproducible measurement of thermal conductivity of molten salts.

THERMAL CONDUCTIVITY – THE BASICS

The thermal conductivity, k, of a material provides information on its ability to conduct heat. A thermal conductivity of 1 W/m·K indicates that an amount of heat of 1 Joule propagates in 1 second through a thickness of 1 m, when the temperature between the two faces is 1 K.

The equation that describes and defines thermal conductivity is known as Fourier’s law for heat conduction, for a one-dimensional case (equation below), where \( q^* \) is the heat flux (W/m²), \( k \) is the thermal conductivity (W/m·K), \( (T_2 - T_1) \) is the thermal gradient (K), and \( x \) is the thickness of the material (m):

\[
q^* = -k \frac{(T_2 - T_1)}{x}
\]

To determine the thermal conductivity, it is necessary to:
- Create a heat flux through the material by using a heat source (e.g., resistor).
- Determine the resulting temperature gradient.
- Solve the heat equation for the specific system/geometry to obtain an expression that links the resulting temperature gradient to the thermal conductivity.

THREE-Omega Technique

3-ω technique: thermal conductivity determination

The 3-omega technique is based on electrically heating a thin planar resistor using an AC harmonic current at a frequency \( \omega \).

\[
\Delta T_{AC} = \frac{2R_0|V_{3\omega}|}{(\partial R/\partial T)|\omega|}
\]

To determine the temperature rise:

\[
\Delta T_{AC} = -\frac{P_{rms}L}{2\pi k l}(2\omega)
\]

where:
- \( P_{rms} \) is the power that drives \( \Delta T_{AC} \)
- \( L \) is the length of the heater
- \( k \) is the thermal conductivity
- \( \omega \) is the frequency

Advantages of the technique

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small sample volume</td>
<td>Perfect for radioactive material</td>
</tr>
<tr>
<td>Fast measurement</td>
<td>Suppress interference from convection</td>
</tr>
<tr>
<td>Direct measurement</td>
<td>Smaller uncertainty than other techniques (e.g., laser flash)</td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS

Thanks to the Pyrochemistry & Molten Salt Systems department and the Glenn T. Seaborg Institute at Idaho National Laboratory. The work is supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract 21P1056-013FP.
Measurement of Heat Capacity and Thermal Conductivity of Molten Salts Using Thermoreflectance

Syed Rizvi, Dr. Alexander Bataller
North Carolina State University, College of Engineering

Introduction

Time-domain thermoreflectance (TDTR) is a method by which the thermal properties of a material can be measured. The main principle behind the technique is that when a material is heated, the change in the reflectance of the surface can be utilized to derive the thermal properties. The reflectivity can be measured as a function of time or frequency, and the data received can be matched to a model with coefficients that correspond to thermal properties.

Method

Fourier’s Law
\[ \frac{\partial T}{\partial t} = \frac{k}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + k \frac{\partial^2 T}{\partial z^2} \]

Thermal properties are extracted by solving Fourier’s law for cylindrically symmetric photothermal deposition.

Result and Discussion

Simultaneous heat capacity and thermal conductivity measurement by creating radial and planar waves

Future Work

Thermal Response:
\[ k = \sqrt{k_C} \]

References

Transport Properties of LiF and FLiBe Molten Salts with DeePot Potentials

Alejandro Rodriguez¹, Stephen Liam², Ming Hu¹

¹Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA
²Department of Chemical Engineering, University of Massachusetts Lowell, Lowell, MA 01854, USA

Access to large-scale simulation with AIMD accuracy
- AIMD scaling with $N^3$, DPSE and RIM (classical) with $N$
- AIMD accuracy + RIM speed = realistic large-scale simulation

Dataset Optimization
- Question: How many DFT is needed for sufficient accuracy?
- LiF Dataset: 118,115 uncompressed/expanded
- FLiBe Dataset: 222,903 uncompressed/expanded
- Test RMSE converges at just 10,000, but poorly represents the predicted density of FLiBe
- Adding >1,000 compressed/expanded structures improves the resulting density

Accuracy to DFT
- LiF RMSE on Testing Set: $2.5 \times 10^{-11}$ eV/atom and 13.8 meV/Å
- FLiBe RMSE on Testing Set: $4.6 \times 10^{-11}$ eV/atom and 22.2 meV/Å
- RMSE co-order of DFT error, yielding excellent representation

Radial Distribution
- The Radial Distribution Function (RDF) describes the concentration of neighboring atoms as a function of radial distance
- Due to ionic nature, molten salts have high characteristic for short-ranged ordering
- The resulting RDF between ionic pairs is computed in DPSE-MD simulation
- Comparison with AIMD shows excellent agreement in representing LiF and FLiBe structure
- Notable disagreement in like-ion pairs is seen in the inset with expansive behavior

Predicted Density
- The low bulk modulus of molten salts yields very sensitive relaxed volumes/densities from DFT
- The predicted density for both LiF and FLiBe are 14% lower than experiment
- Several factors:
  1. Lack of long-ranged coulombic interactions
  2. No van der Waals interactions included in DFT data
  3. More testing needed on pseudopotential is required
- Highlight the importance of density capture in predicting subsequent properties

Thermal Conductivity
- Equilibrium Molecular Dynamics with Green-Kubo (EMD-GK) is performed
- Good agreement to experiment for simulation at experimental density and relaxed density
- Phenomenological contribution to thermal conductivity is considered: $\kappa = \frac{1}{3} \frac{T^2 L}{E_{22} E_{33}}$
- Difference between experimental density and relaxed density is considerable

Electrical Conductivity
- Electrical conductivity is higher at experimental density than a relaxed density
- This is despite the higher ionic mobility in the relaxed density case
- Insets show extensive electrical conductivity with overlap in both cases
- Larger volume reduces the KC in the GK formulation

Diffusion Coefficient
- The Diffusion Coefficient describes the mobility of ions in the molten salt
- Notably, high Li+ mobility is seen in both LiF and FLiBe
- F- mobility is reduced from LiF to FLiBe due to tetrahedral BeF formation
- Mobility of ions increases generally with relaxed supercell (dashed line)
- Agreement with experiment shown as symbols

Shear Viscosity
- The shear viscosity at experimental represents agreement accurately
- The viscosity at relaxed density is consistently lower, reflective of higher ion mobility
- In general, the Arrhenius nature with temperature is captured, especially in FLiBe

Alejandro is supported by award # DE-NE-0000095, Stephen Liam supported by award # DE-NE0009204
Applications of Thermochimica for Molten Salt Systems

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Ontario Tech University, Oshawa, Canada.
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**Thermochimica**

Thermochimica [1] is an open-source equilibrium thermodynamics software library that solves for a unique combination of phases and concentrations that minimizes the Gibbs energy of an input system. This is performed using the Gibbs Energy Minimization (GEM) method [2]. Upon successful optimization of the chemical system, many thermochimical properties are available, including the masses of stable phases, the concentrations of all species in every stable solution phase, the Gibbs energy of the system, and the chemical potentials of all system components and stable species in the system.

**Modified Quasi-chemical Model**

The MQMQA [3, 4, 5, 6, 7] is a thermodynamic model for treating Short-Range Order (SRO) with two sublattices. MQMQA is commonly used to represent molten salts. This model has recently been implemented in Thermochimica [8].

**Verification**

To verify the accuracy of MQMQA calculations in Thermochimica, direct benchmarking comparisons were made with the commercial software FactSage [9], using the molten salt thermodynamic database (MSTDB) [10]. These calculations include complex nuclear fuel salt mixtures.

**Phase Diagrams**

Thermochimica is now able to generate phase diagrams, which can be used to ensure that reasonable output is provided for well-understood molten salt systems.

**Thermochimica – TRANSFORM Coupling**

A TRANSFORM [11, 12] model of the primary fuel and coolant loops of the MDR was modified to include new Thermochimica-driven mass accountancy components. The initial composition of the salt was 41.89% LiF, 10.36% NaF, 37.84% KF, 4.50% UF₄, 4.50% UF₃, and 0.90% PuF₃ (mole fractions). Under normal operating conditions, collected masses of all elements were less than 0.1 g out of the total 111,880 kg total mass of the salt, and consisted almost entirely of KF.

The primary coolant loop pump flow rate was reduced to 5% of its initial value over the course of 25,000 s, beginning at 50,000 s. The reduction in flow rate caused less cooling of the primary fuel loop at the heat exchanger. This represents a possible loss-of-coolant accident (LOCA) scenario. During this accident scenario, no significant release of material was predicted by the model. These results are likely to be significantly different given a more complete thermodynamic database. Specifically, it is expected that noble gases such as Kr and Xe would likely dominate the off-gas that is removed.

**Thermochimica – MELCOR Coupling**

Integration of Thermochimica in the severe accident modeling code MELCOR [13] is underway. Thermochimica will provide outputs such as partial pressures of gas species for source term analysis.

Preliminary analysis of Cs release from molten salt cooled TRISO during LOCA sequence is shown below, courtesy of SCALE/MELCOR staff and U.S. NRC.

**Conclusion**

The implementation of MQMQA in Thermochimica has enabled many applications to simulations of molten salts, including nuclear fuel salt systems with fission and activation products. These developments make Thermochimica the first open-source and readily couplable thermochemistry library to support the MQMQA. Thermochimica has been coupled to the dynamic systems modeling library TRANSFORM for simulations of molten salt reactor operations, including potential accident scenarios.

Integration of Thermochimica in the severe accident code MELCOR is underway. Thermochimica will provide input for source term analysis in MELCOR.

**Acknowledgement**

This work was funded in part by the Department of Energy Nuclear Energy Advanced Modeling and Simulation program.

This research was undertaken, in part, thanks to funding from the Canada Research Chairs (950-231328) program of the Natural Sciences and Engineering Research Council of Canada.

Thanks to Scott Greenwood at ORNL for collaboration on TRANSFORM coupling.

Thanks to Fred Gelbard and David Luxat at SNL for collaboration on MELCOR coupling.

**References**


[3] A. Pelton, S. Degterov, G. Eriksson, K. Back, R. Mahdavi, J. McManus, A. Pelton, and S. Peterson, "CALPHAD: a possible loss-of-coolant accident (LOCA) scenario. During this accident scenario, no significant release of material was predicted by the model. These results are likely to be significantly different given a more complete thermodynamic database. Specifically, it is expected that noble gases such as Kr and Xe would likely dominate the off-gas that is removed.

**Thermochimica GUI**

A graphical user interface for Thermochimica has been developed to simplify standalone use. The interface allows for a series of calculations in temperature or pressure to be run. Separate GUIs are available for plotting results and generating phase diagrams.

**REFERENCES**


[3] A. Pelton, S. Degterov, G. Eriksson, K. Back, R. Mahdavi, J. McManus, A. Pelton, and S. Peterson, "CALPHAD: a possible loss-of-coolant accident (LOCA) scenario. During this accident scenario, no significant release of material was predicted by the model. These results are likely to be significantly different given a more complete thermodynamic database. Specifically, it is expected that noble gases such as Kr and Xe would likely dominate the off-gas that is removed.

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Purification of Uranium Tetrafluoride via Solid-state Reaction with Ammonium Bifluoride

Kyle Foster1, Juliano Schorne-Pinto1, Bernie Fitzpatrick2, Markus Pro2, Theodore Besmann1

1University of South Carolina, Department of Mechanical Engineering
2Ontario Tech University, Department of Nuclear Engineering

Objective:

Purify as-received uranium tetrafluoride using ammonium bifluoride in a closed system with a high degree of reproducibility.

Methodology

- 1:2 NH4HF2 : UF4 by mass
- Mixed thoroughly using mortar and pestle in Ar filled glovebox
- 2-stage heating process with 100˚C low dwell period and 480˚C high dwell period
- Open vessel reaction to avoid formation of nickel (II) fluoride
- Analyzed using DSC, XRD, and ICP-OES

Reaction System Components

- Reaction Vessel
  - Sealed Ni reaction vessel sourced from Parr Instruments
  - Internal graphite crucible with lid contained samples
  - Ar continuously flown through the vessel following being cleaned by a Setnag Gen’Air HF Removal
  - Off-gas was flown through three in-series impingers filled with KOH to scrub HF gas

- Heating and Insulation
  - Heating provided by a BriskHeat SAMOX heating tape with SDC temperature controller with a built-in J-type thermocouple
  - Insulation provided by mineral wool pipe insulation and a ½” calcium silicate base plate

Conclusions

- Improvement in salt purity (oxygen removal) shown by over 100˚C improvement on DSC measurement of melting peak and onset temperature
- Consistently reproducible process over multiple trials
- Enables purification of UF4 without the use of a costly and hazardous HF line
- Improved crystallinity in purified samples
- Melting behavior most dependent on high temperature duration

Funding by U.S. Department of Energy Office of Nuclear Energy, Nuclear Energy University Programs, and the MSTDB-TC development effort under the Nuclear Energy Advanced Modeling and Simulation Program administered by Los Alamos National Laboratory, which is operated by Triad National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract number 89233218NCA000001.

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Ca 317.933 (mg/L)</th>
<th>Al 391.513 (mg/L)</th>
<th>Fe 238.284 (mg/L)</th>
<th>U 385.958 (mg/L)</th>
<th>Mg 285.213 (mg/L)</th>
<th>Ni 231.604 (mg/L)</th>
<th>Sr 407.771 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 UF4-ORNL</td>
<td>0.226</td>
<td>0.001</td>
<td>0.005</td>
<td>4.475</td>
<td>0.005</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>2 UF4-Bioanalytics</td>
<td>0.297</td>
<td>0.002</td>
<td>0.000</td>
<td>2.661</td>
<td>0.001</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>3 UF4-Purified</td>
<td>0.273</td>
<td>0.007</td>
<td>0.005</td>
<td>4.757</td>
<td>0.009</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>4 Water+AR</td>
<td>0.198</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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</tr>
<tr>
<td>5 Water+HCl</td>
<td>0.167</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>6 Water+HNO3</td>
<td>0.164</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Shown is the DSC curve of as-received UF4.
Molten salt reactor developers require viscosity values of fuel and coolant salts to predict fluid flow rates and needed pumping power under operating and accident conditions. Viscosity values for many of the proposed salt compositions are either unavailable or conflicting. Thus, high quality viscosity data are needed to support the licensing and operation of these reactors.

Scatter in measured FLiNaK viscosity values highlights the need to understand factors affecting measurements, including salt composition, system geometry, turbulence, fluid volume, and impurities (e.g., undissolved solids). This work summarizes the effects of geometry, turbulence, and fluid volume on viscosity.

EFFECT OF FLUID VOLUME

The volume of fluid above and below the immersed spindle is expected to affect the measurement. These effects were evaluated through a series of measurements with the spindle immersed at different depths within silicone oil. The calculated viscosity increases as the bottom of the spindle approaches the bottom of the crucible (shown) and as the volume of fluid above the spindle increases (possibly due to increased motor shaft length immersion).

CONCLUSION

The effects of geometry, turbulence, and fluid volume on viscosity measurements using a rotational viscometer have been identified and controls implemented to provide high quality measurements of molten salt viscosity.

ACKNOWLEDGMENTS AND FURTHER INFORMATION

This work has been funded under the DOE MSR campaign. For more information about viscosity measurements at Argonne National Laboratory, contact Melissa Rose at mrose@ornl.gov.

REFERENCES

Lack of information for AkCl-AnCl₃ systems

There is a lack of information on the mixing enthalpy (Δ_{mix}H) for many lanthanide and other important salt systems because of the experimental challenge in measuring these values. Thus, a straightforward methodology for predicting Δ_{mix}H would be of great value to inform development of thermodynamic descriptions through the CALculation of PHase Diagram (CALPHAD) approach.

Background and data mining

Davis’ theory: Δ_{mix}H is described as a function of an interaction parameter λ^M that varies linearly with respect to a size parameter δ_{12} at constant temperature (or neglectable Δν), composition and pressure.

\[ \lambda^M = \frac{\Delta_{mix}H}{X_{AkCl}X_{MCl_3}} \]
\[ \delta_{12} = \frac{(r_{Ak}^+ + r_{Cl}^-) - (r_M^+ + r_{Cl}^-)}{r_M^+ + r_{Cl}^-} \]

\[ (r_{Ak}^+, r_{Cl}^-) \text{ are the ionic radii of the alkali, lanthanide/actinide, and chlorine, respectively, from values in the octahedral geometry compendium of Shannon.} \]

Data mining: The experimental data of Δ_{mix}H for alkali chloride mixtures with lanthanane (and yttrium) trichlorides are abundant in the literature. In this work we compiled 48 sets of data to construct our analysis measured between 1044–1263 K for LaCl₃ (1.032 Å) to YbCl₃ (0.868 Å).

The alkali chloride melts with CeCl₃ offer a very good example of the behavior of AkCl-MCl₃ systems, where M is a lanthanide or actinide. The Δ_{mix}H values are negative, and becomes more negative with increasing alkali radius.

Data fitting and short-range ordering

Data fitting: The composition at maximum SRO was determined for each system of 48 mined sets by regression of the Δ_{mix}H functions using the Surrounded Ion Model.

\[ \Delta_{mix}H = [(1-x)pq + xrs] \sqrt{(1-(1-x)(f_1 + f_2x + f_3x^2)} \]
\[ x' = \frac{[1-(1-x)pq + xrs]}{x} \]

where p = q = s = 1, r = 3, and f are fitting coefficients.

Short-range ordering: A linear behavior of SRO vs δ_{12} allows reasonably accurate interpolation of the composition at maximum SRO for systems lacking such values. As that is the case for uranium- and plutonium-containing systems:

Our method improves upon previous empirical approaches by eliminating the need for arbitrarily choosing the required composition at maximum short-range ordering, the minimum Δ_{mix}H, prior to performing the estimation.

Otherwise, estimation of Δ_{mix}H at any composition other than the composition of maximum SRO creates ambiguity, here showed for a selection of the equimolecular composition for asymmetric halide salts.

Validation of the method

We intentionally omitted NaCl-UCl₃ set in our SRO prediction, and we use this value to predict the Δ_{mix}H using Davis’ method in quadratic approximation with very good agreement:

Predictions for AkCl-An/LnCl₃ + CALPHAD

Predictions for unexplored systems: Encouraged by the comparative results for the NaCl-UCl₃ system, our methodology was applied to the remaining alkali-uranium and -plutonium chloride systems. We also did predictions of enthalpy of mixing for 27 unexplored AkCl-LnCl₃ systems: LiCl-PmCl₃, LiCl-SmCl₃, LiCl-EuCl₃, LiCl-DyCl₃, LiCl-HoCl₃, LiCl-ErCl₃, NaCl-PmCl₃, NaCl-EuCl₃, NaCl-HoCl₃, KCl-PmCl₃, KCl-SmCl₃, KCl-EuCl₃, KCl-HoCl₃, KCl-ErCl₃, RbCl-PmCl₃, RbCl-ErCl₃, CsCl-PmCl₃, CsCl-SmCl₃, CsCl-EuCl₃, CsCl-DyCl₃, CsCl-HoCl₃, CsCl-ErCl₃, and CsCl-UCl₃.

Thermodynamic assessment of NaCl-PuCl₃: The methodology for determining Δ_{mix}H is used in CALPHAD modeling of the NaCl-PuCl₃ system to provide an example of its utility.

Conclusions

In this work, which is a paper under review, we have developed a correlational approach to estimate the composition of maximum SRO at which Δ_{mix}H is most negative. Additionally, the correlation captures the errors of available experimental data and propagates them to predicted values. As experimental measurements of Δ_{mix}H are often unavailable or difficult to obtain, the demonstrated relations and developed methodology meet a critical need for efficiently generating thermodynamic properties of molten salts.

Acknowledgements

This research was supported by the National Energy Advanced Modeling and Simulation Program administered by Los Alamos National Laboratory, which is operated by Triad National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract number 89233218NCA0000001.
DSC measurements for molten salts: zero rate method coupled with error propagation & examples of interpretation of complex phase transitions
Jacob A. Yingling, Juliano Schorne-Pinto, Clara M. Dixon, Mina Azizilha, Theodore M. Besmann

**Single rate DSC calibration is error prone**

Practical DSC measurement have expected variations:
- Sample mass and thermal conductivity.
- Thermocouple asymmetry and DSC system resistance. These effects result in variations that are inconsistent even for the same heat rate.
- DSC calibration at a single heat rate cannot compensate for these errors.

**Stoichiometric compound stability problem**

Contradictory phase diagram data have been published for KCl-UCl₃ system.
- Some measurements indicate surprisingly flat liquidus in the range x(UCl₃) = 0.3 to 0.48.
- Our own measurements show complicated eutectic behavior with a strong “liquidus” near the melting point of K₂UCl₅.

**DSC ran using KCl-UCl₃ mixture**

x(UCl₃) = 0.419

- Using IUPAC DSC measurement helps to identify rate dependent kinetic effects in the salt mixture.
- Endothermic events near 590°C are not observable at high heat rates (10 K/min) common for DSC measurements in the literature.

**Sample annealing confirms liquidus**

Sample x(UCl₃)=0.419 was remeasured after quenching and annealing to improve the liquidus measurement.
- Post-treatment measurement exactly confirms measurements by Suglobova.
- Untreated measurement at x(UCl₃)=0.575 may indicate high-temperature phase common to other KCl-lanthanide systems.

**Mole fraction of UCl₃**

<table>
<thead>
<tr>
<th>Mol fraction of UCl₃</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.329</td>
<td>Kraus (1943)</td>
</tr>
<tr>
<td>0.419</td>
<td>Suglobova et al. (1981)</td>
</tr>
<tr>
<td>0.575</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Conclusions**

- IUPAC zero rate calibration minimizes errors inherent in DSC extrapolated onset measurements.
- Linear error propagation applied to DSC calibration is an effective means of determining individual measurement uncertainty.
- Stoichiometric compound stability may result in misleading DSC signals that have been misidentified as the liquidus in recent literature. Sample annealing prior to measurement improves equilibrium condition and reveals the real liquidus signal.

**Acknowledgements**

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**References**

Progress in Coupling Thermochimica and OpenFOAM for MSR Applications

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Introduction

Computational Fluid Dynamics (CFD) can be coupled to Computational Thermodynamics (CT) codes to develop an innovative capability for molten salt reactor applications. This study aims to show a demonstration problem for molten salt reactor (MSR) applications through a one-way coupling between OpenFOAM (CFD) and Thermochimica (CT) libraries. The ultimate goal is to demonstrate a two-way coupling for a more accurate and complex analysis.

Methodology

A one-way coupling between both codes is represented by the flowchart below. OpenFOAM provides temperature and pressure from the CFD simulation. From the chemistry perspective, the element mass from the desired chemical composition and the Gibbs Energy Functions for the thermodynamic equilibrium calculation need to be provided.

Such functions are available from a designated nuclear material database. In this case, from the JRC Molten Salt Database (JRCMSD). Thermochimica calculates the chemical equilibrium through a Gibbs Energy Minimizer method and provides the following post-process thermophysical properties in the green charts.

Through a C++ I/O stream script, the inputs are read and written and then undergo post-processing in the open-source Paraview visualization software.

Molten Salt Composition

The binary phase diagram of LiF-CsF is illustrated below and was calculated using FactSage 7.3 and the JRCMSD.

![Diagram of Molten Salt Composition](image)

Time = 1 s  Time = 500 s

Partial Pressure of CsF

The partial pressure of CsF is calculated through the one-way coupling and is illustrated below. OpenFOAM was set to calculate a single-phase homogeneous phase, but Thermochimica is telling the existence of three phases and also the production of 75 kPa of CsF through the green line contour.

![Diagram of Partial Pressure of CsF](image)

One-Way Coupling Results: OpenFOAM + Thermochimica

To illustrate the results for this demonstration problem, the temperature and mol fraction of ideal gas contour plot is illustrated below.

![Diagram of One-Way Coupling Results](image)

Conclusions

This one-way coupling demonstration problem showed a good agreement between the temperature and the binary phase diagram. The final intent is to demonstrate a two-way coupling between both codes for more complex analysis and geometries. However, this first step already showed the possibilities for molten salt reactor applications.

Acknowledgments

This research was undertaken, in part, thanks to funding from the Canada Research Chairs program (950-231328) of the Natural Sciences and Engineering Research Council of Canada. This project is in support of the SAMOSAFER project. Finally, we would like to acknowledge the contribution from Ondrej Benes from JRC in this project.