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PNNL

Molten Salt Reactor PROGRAM

Thermophysical Properties of Fuel and Coolant Salt Compositions

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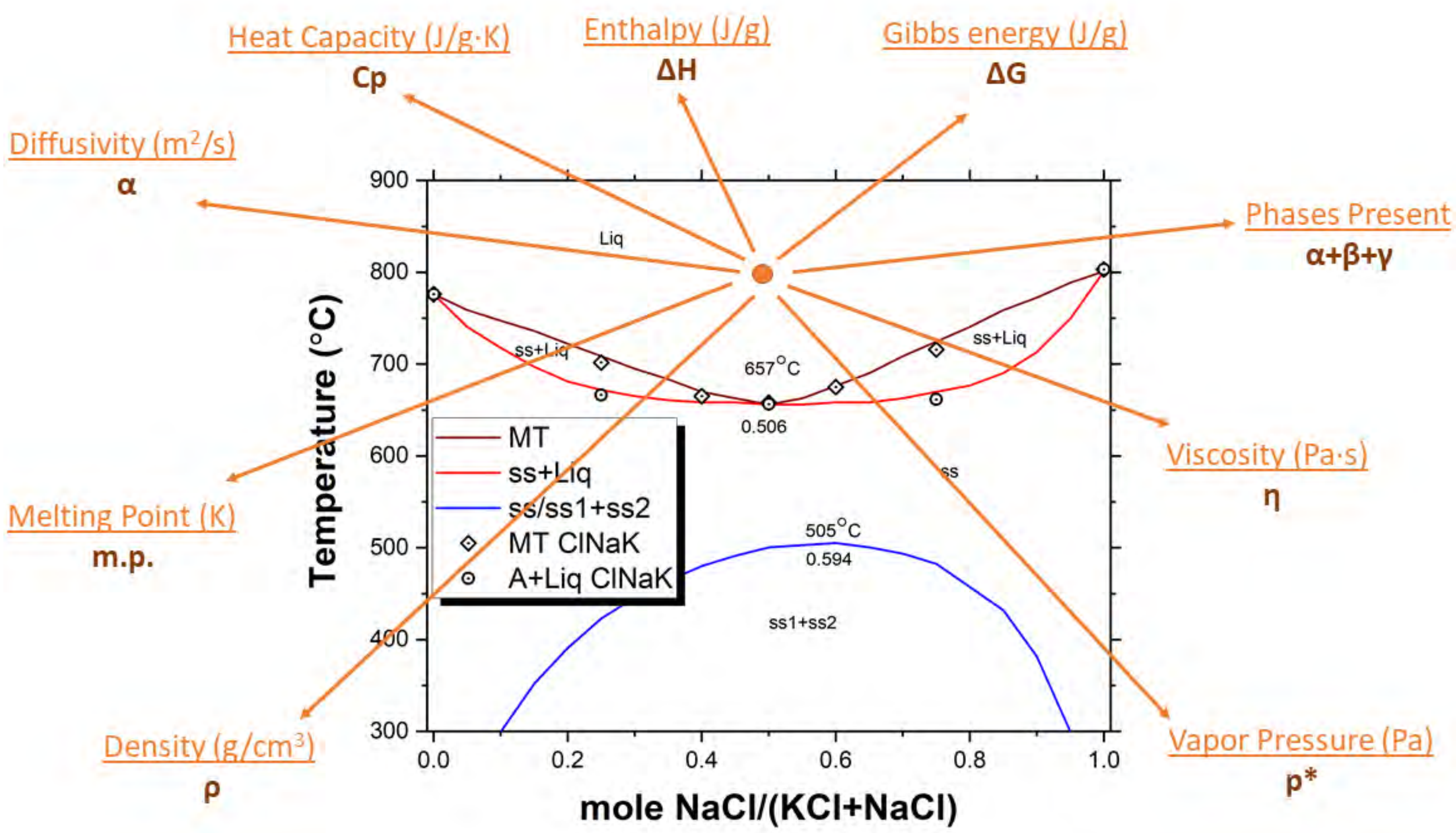
Annual MSR Campaign Review Meeting 2-4 May 2023

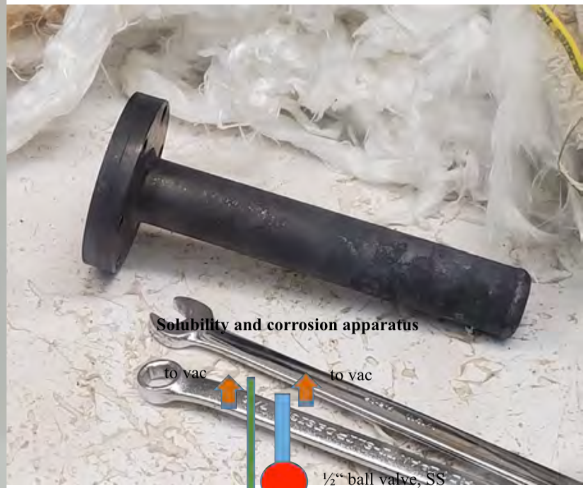
Goal: Provide Data to Support MSTDB

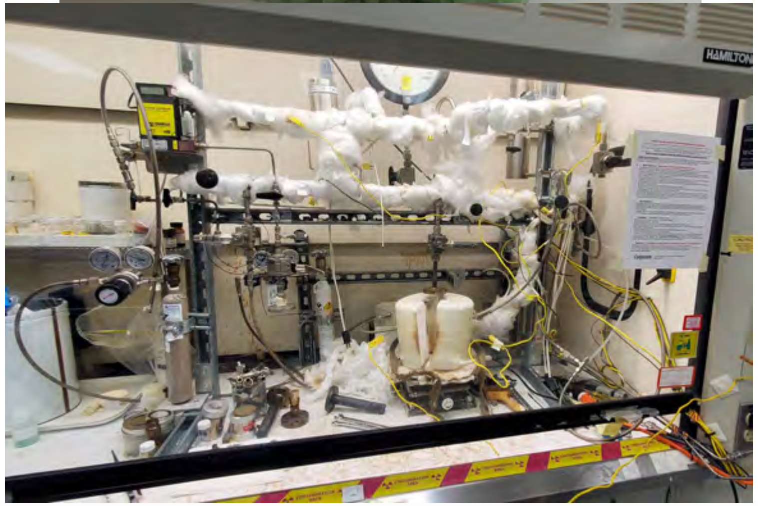
- Use PNNL, WSU, and CSU thermophysical properties expertise to build and modify thermal measurement systems.
  - ➢ Density (Pycnometry): Online/Dev
  - ➢ Heat Capacity (DSC, Drop Cal): Online
  - ➢ Enthalpy of Fusion (Drop Cal): Online
  - ➢ Viscosity (TMA): In development
  - ➢ Melting Point (TMA, DSC): Online
  - ➢ Vapor Pressure (TGA-DTA): Online/Dev
  - ➢ Thermal diffusivity (Laser Flash): Need Equipment/Development
  - ➢ Emissivity (pyrometer): Online/Dev
- FY23 Milestones
  1. Density and viscosity capability development.
  2. Thermophysical property data collection and reporting.
  3. Coolant salt testing (NaCl-KCl, $NaCl\text{-}MgCl_2$)
  4. Fuel salt testing ($LiF\text{-}UF_4$, $NaCl\text{-}UCl_3$)

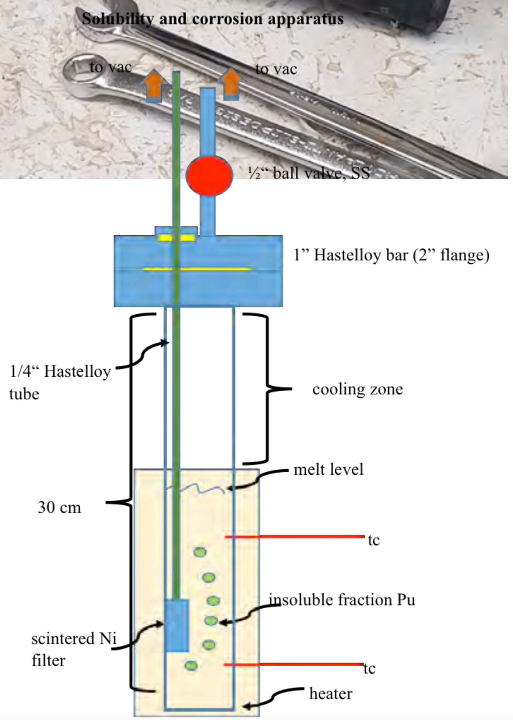


Synthesis & Purification

- **Synthesis:**
  - Currently set up to use CCl_4, Cl_2, HCl, H_2, and HF on U (<100 g) and Pu (~5 g).
  - Other reagents can be added with quick turn around.
  - Current synthesis is Schlenk-line type system in a radiological fumehood (FH).
    - ➢ Normal limits for Pu in rad FH are ~10 mg.
    - ➢ We load and unload in non-inert glovebox (GB).
  - Inert GB work in RPL online.
    - ➢ (10-100 g Pu).
- **Purification:**
  - For OH_x.
    - ➢ High temp vacuum heating (10^{-5} torr, >400 ºC) is simplest.
    - ➢ Halogenation (requires H_2 due to HF/HCl solubility or He* sparging).







Storage & Batching

- 99.99%+ pure ultra dry Cl powders (Alfa Aesar) are shipped and stored in controlled environment conditions.
  - UCl_3 from TerraPower.
- 99.99%+ pure dry F powders (Sigma Aldrich) are stored in controlled environmental conditions.
  - UF_4 synthesis in house.

- Batching performed in a negative pressure, inert atmosphere workstation to keep salts pure.

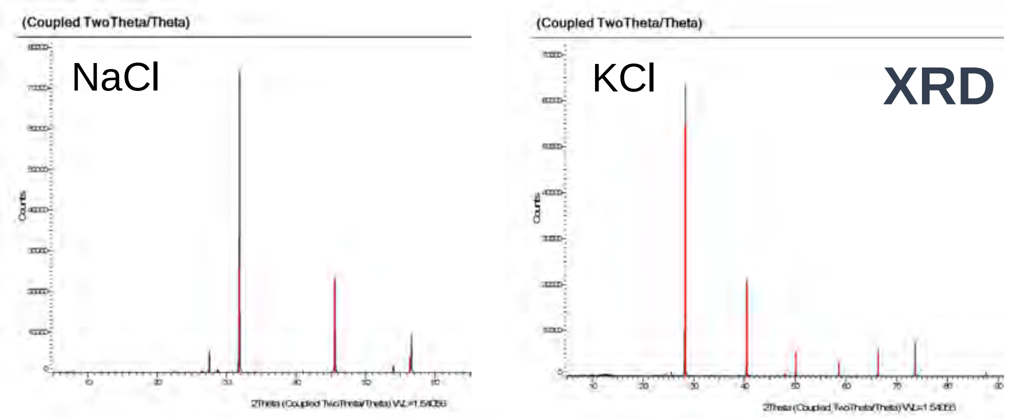
- 5 – 100 grams of a given salt composition are prepared at a time, typically the whole series is batched in a day.

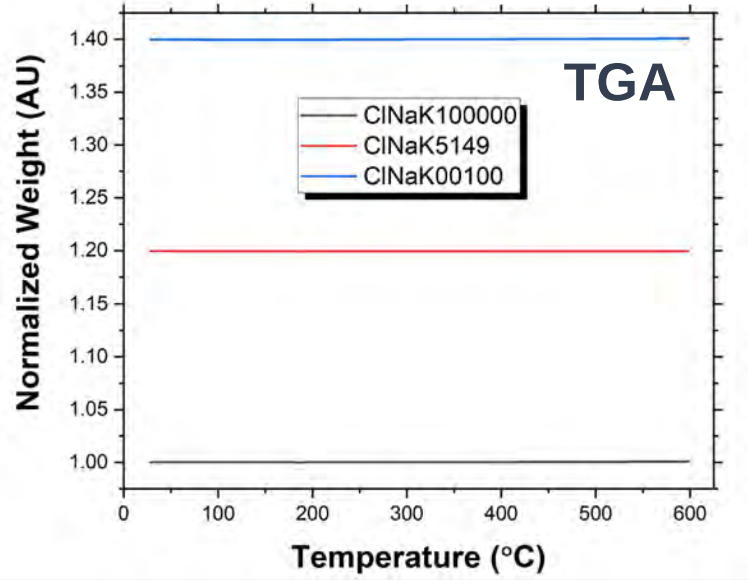
- Each sample is mixed using a mortar and pestle for 10 minutes to ensure uniformity.

Characterization (TGA & XRD)

- XRD & TGA analysis is used a rough characterization of salts.
  - ➢ Cl & F powders are surprisingly dry
    - o No mass change during TGA under 400°C.
  - ➢ NaCl, KCl, $MgCl_2$, LiF, NaF & UF_4 are free of large (2%+) elemental contamination.
    - o Only source compound identified by XRD.

➢ No metals, water, or hydroxyl groups seen during analysis.





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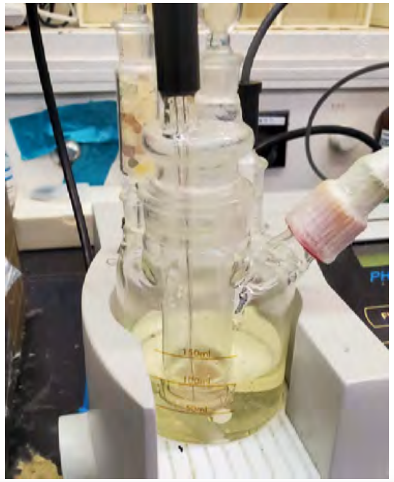
Characterization (Karl Fischer Titration)

- KF Titration is used a precise characterization of water content.
- Many F and Cl salts can be highly hygroscopic.
- How to determine minor or trace water present?
  - ➢ KF Titration can measure single ppm levels of water content.
- Our ultra dry and high purity Cl salts from the manufacturer contain between 0.1-0.5 wt% H_2O.
  - ➢ How does this affect thermal properties, stability, and corrosion?
  - ➢ How dry is dry enough?



$$H_2O + SO_2 + I_2 \rightarrow SO_3 + 2\,HI$$

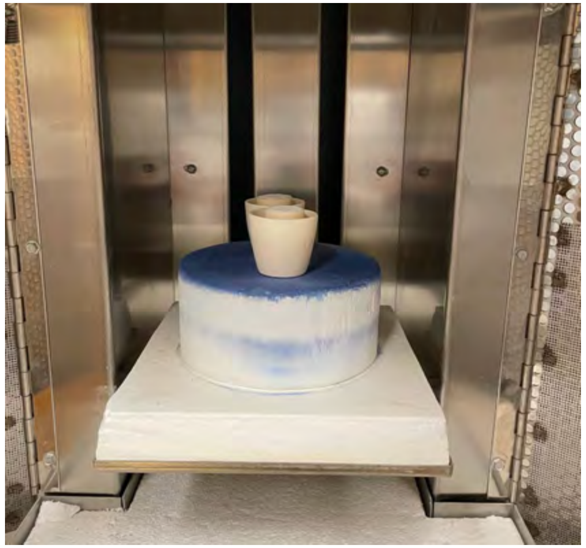
$$2I^- \rightarrow I_2 + 2e^-$$

Notes	Salt	Vendor	Sample Mass mg	Water Mass µg	Water Concentration wt.%
Ultra Dry Powder stored in inert glove box	100% KCl	Alfa Aesar	112.2	145	0.13
Ultra Dry Powder stored in inert glove box	25% NaCl - 75% KCl	Alfa Aesar	107.5	294.3	0.27
Ultra Dry Powder stored in inert glove box	51% NaCl - 49% KCl	Alfa Aesar	103	149	0.14
Ultra Dry Powder stored in inert glove box	75% NaCl - 25% KCl	Alfa Aesar	135.1	207.8	0.15
Ultra Dry Powder stored in inert glove box	100% NaCl	Alfa Aesar	118.7	122.5	0.10
High metals purity powder stored on lab shelf	100% KCl	American Elements	105.9	845.9	0.08
High metals purity powder stored on lab shelf	100% NaCl	American Elements	139.3	1099.7	0.09
Ultra Dry Powder cleaned in flowing salt loop	57% NaCl - 43% MgCl2	TerraPower	108.3	152.5	0.14
High metals purity powder stored on lab shelf	100% MgCl2	Sigma Aldrich	110.3	3051	0.55

Liquid Density (Pycnometry Approach 1)
Ceramic Crucibles

Experimental setup

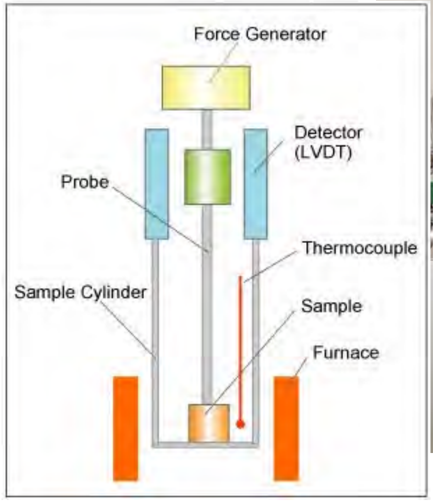
- Weigh an alumina crucible and measure the dimensions with calibrated calipers.
- Pack with sample powder.
- Place crucible into overflow crucible and into the furnace.
- Ramp rate of 10°C/min to desired temperature
- Held at temperature for two to three hours
- Clean any overflow and take mass with and without residual.



Liquid Density (Pycnometry Approach 2) Thermomechanical Analysis (TMA)

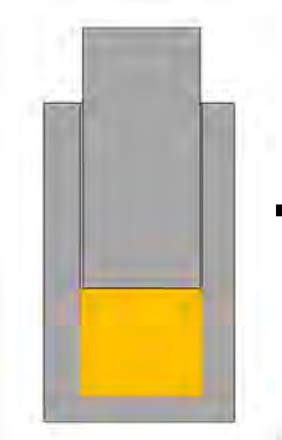
Experimental setup

- The salts are placed in a fixed diameter crucible.
- The probe is set to press on the salts with a fixed or modulated force.
- As the salts expand or contract the LVD
  measures the one-dimensional motion with temperature.
  - ➢ This movement can be used to determine thermal expansion, viscosity, density and phase changes.



Density Equation

$$\rho = \frac{m_f}{V_i}$$



$$\xrightarrow{\Delta T}$$

$$\Delta V = \pi r^2 \Delta h$$

Density NaCl-KCl (AIMD Modeling)

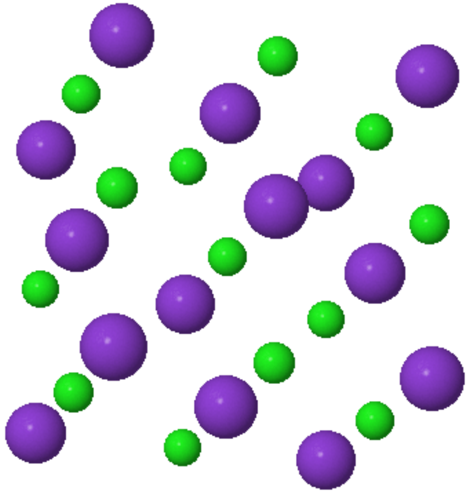
Computational Method

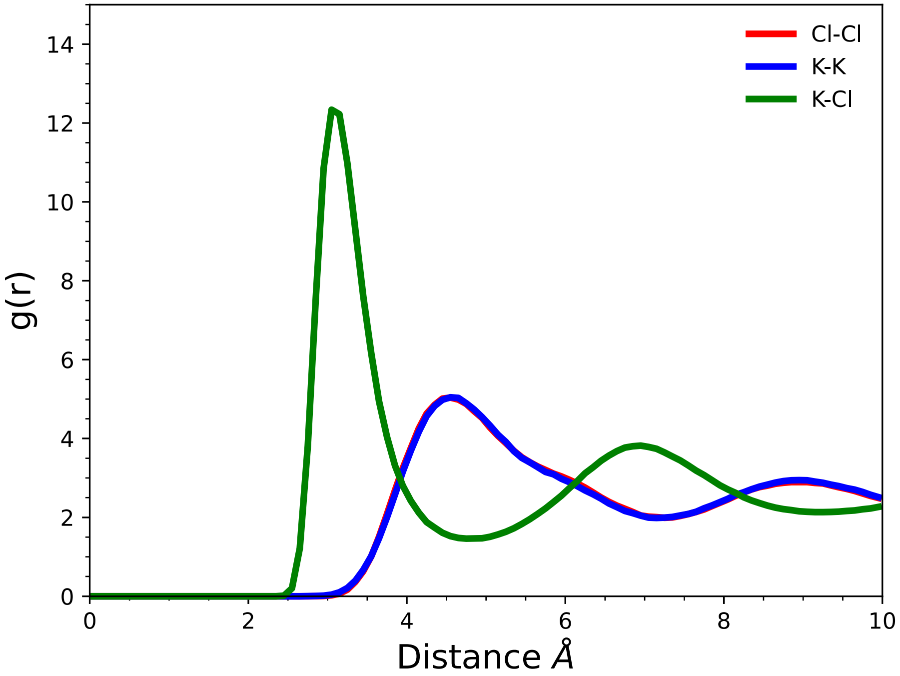
- Ab-initio molecular dynamics (AIMD) as implemented in CP2K[1]
- Single-zeta basis set with the exchange correlation approximated using PBE functional
- Density calculation (ρ):

$$\rho = \frac{NM}{N_a V}$$

- Radial distribution function (g(r)):

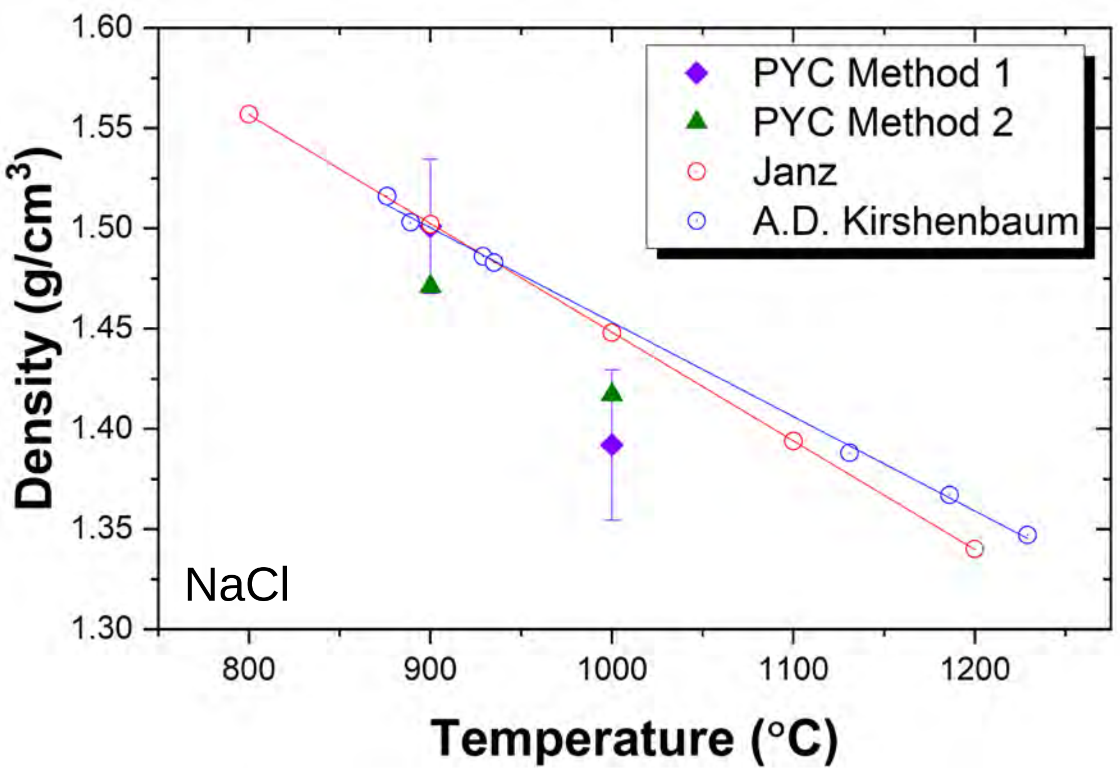
$$g_{ij} = \frac{1}{4\pi\rho_j r^2}\left[\frac{dn_{ij}(r)}{dr}\right]$$

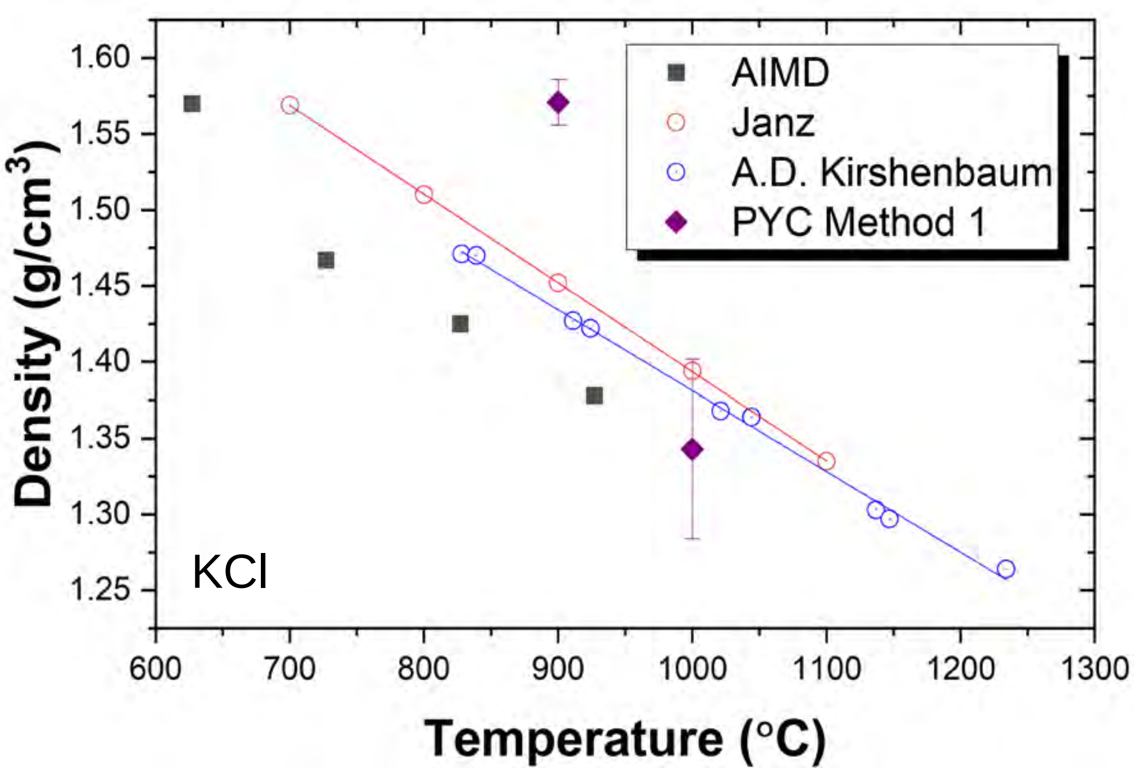




- Temperature has negligible effect on local structure, which is observed in other molten salt studies[1]

Liquid Density Results





- Experiments on pure NaCl and KCl are underway.
  - ➢ Initial results compare reasonably well to literature.
- Future work on fine tuning method, expanding temperatures tested, and expanding testing matrix.

- AIMD model are in reasonable agreement with literature.
  - ➢Deviations possibly due to exchange-correlational approximations.

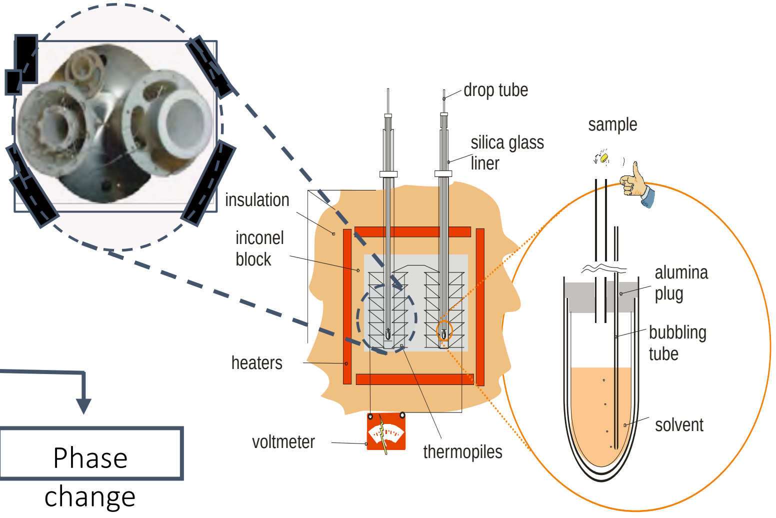
Twin Calvet Drop Calorimetry

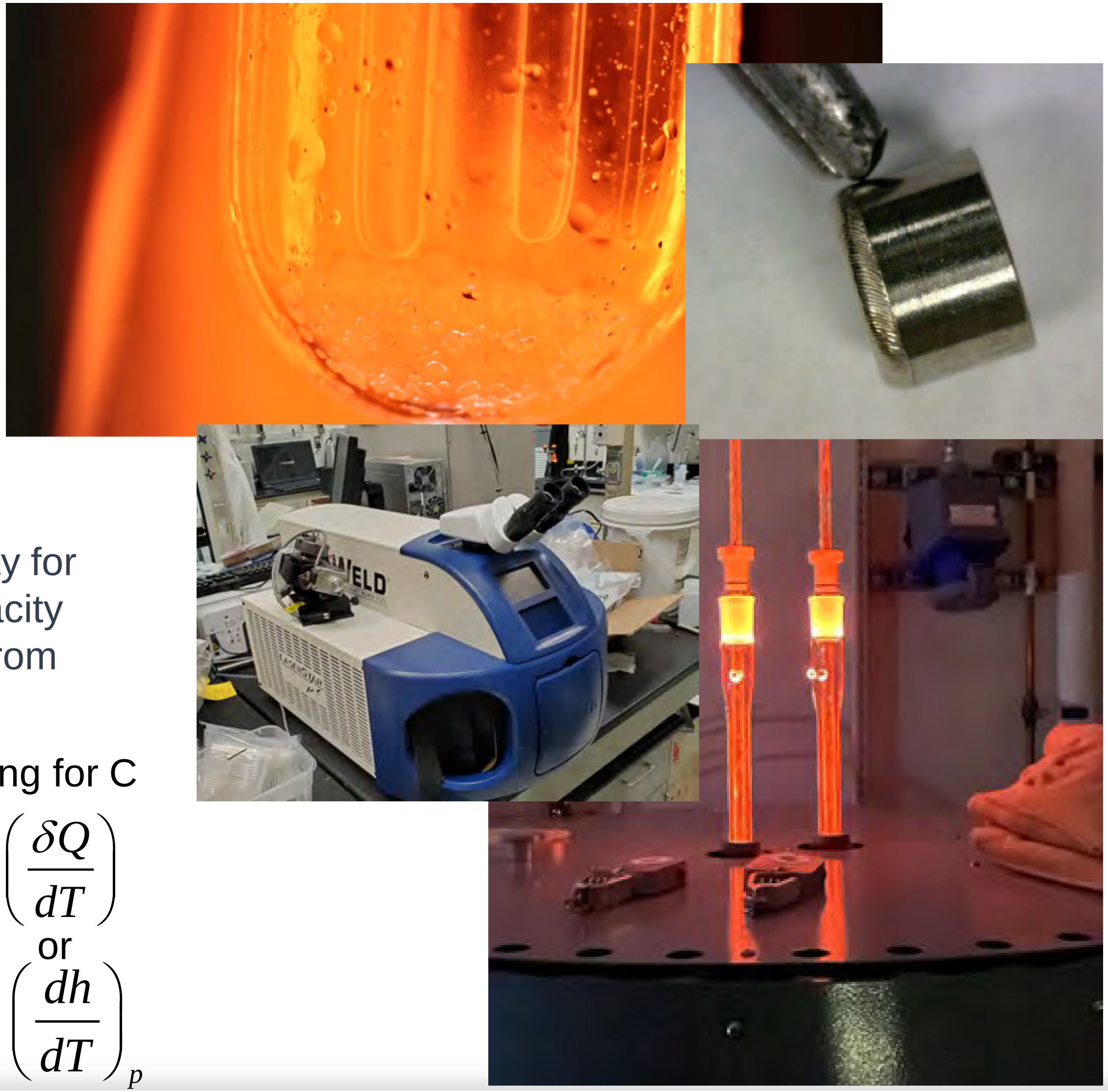
$\Delta H, C_p$

Produced enthalpy data:

$\Delta H_{ds} = \Delta H_{hc} + \Delta H_{rxn} + \Delta H_{ph}$

Heat content | Reaction | Phase change





Calculating heat capacity from enthalpy:

This instrument gives us the capability for very accurate and precise heat capacity measurements of materials above from ~25 - 1000°C

1) First law of thermodynamics

$$Q = C\Delta T$$

and

$$dH = \delta Q + Vdp$$

2) If we have constant pressure

$$Vdp = 0$$

therefore

$$dH = \delta Q$$

3) Solving for C

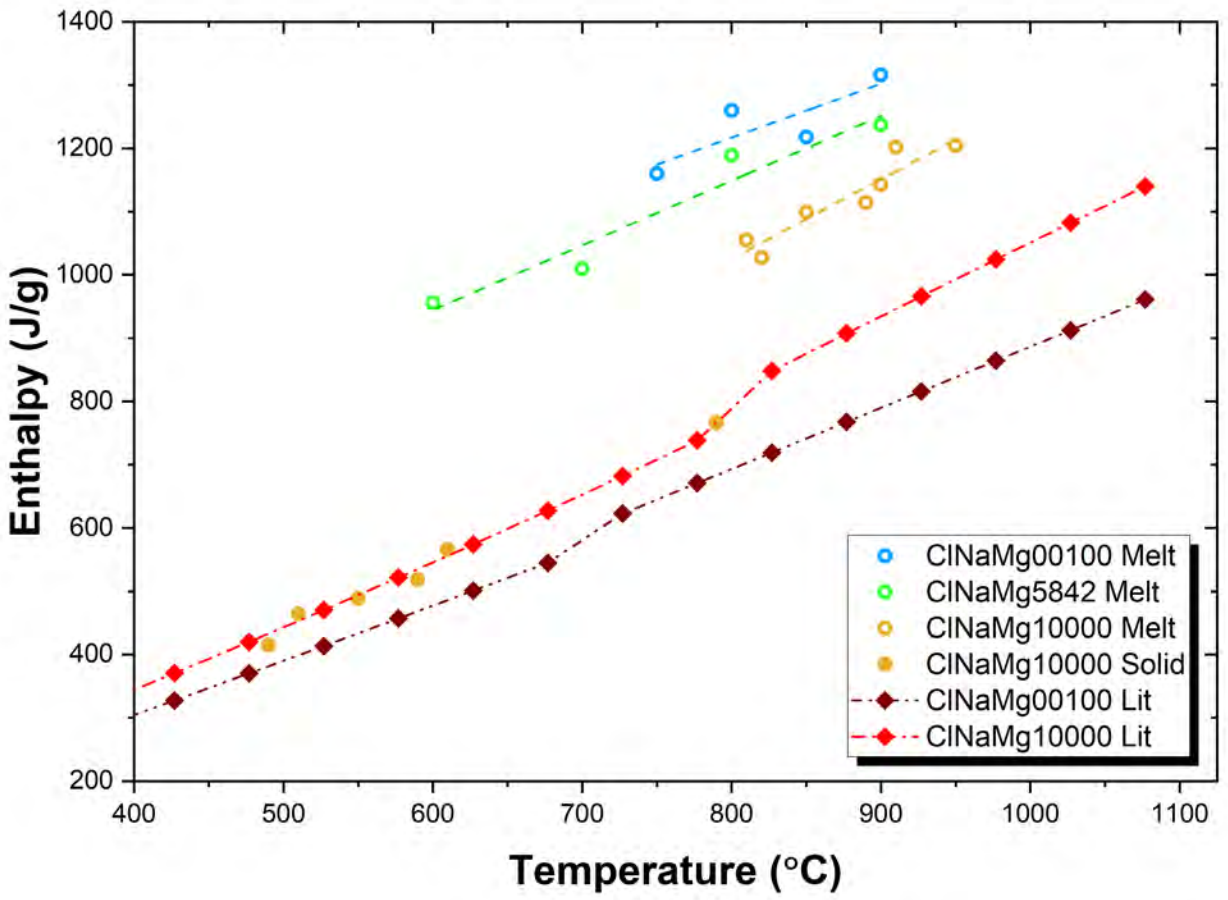
$$C_p = \left(\frac{\delta Q}{dT}\right)$$

or

$$C_p = \left(\frac{dh}{dT}\right)_p$$

Enthalpy of $NaCl$-$MgCl_2$-UCl_3 System

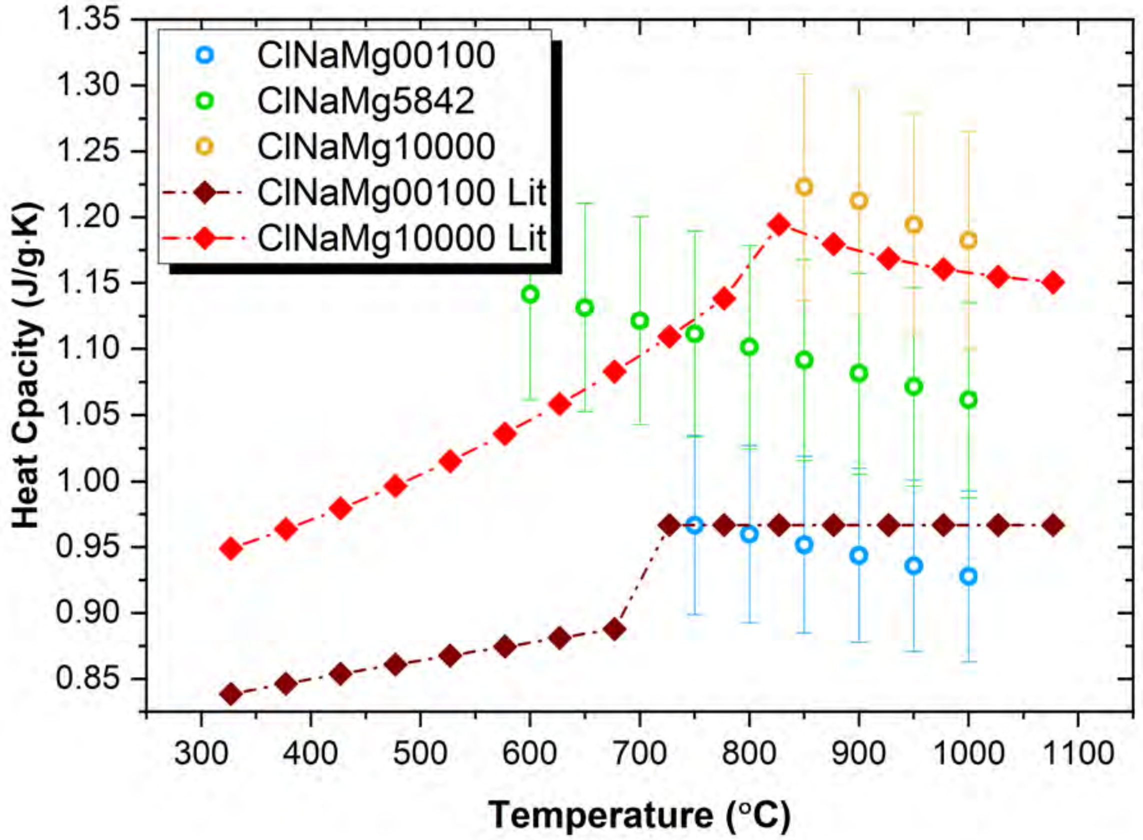
$\Delta H, C_p$



- Values range from 415 J/g at 490°C to 1316 J/g at 900°C.
- Enthalpy increases with temperature for all compositions.
- Solid state measurements match well with NIST JANAF literature.
- Liquid state measurements show an increase in values and separation between endpoints.
    - Due to vapor phase (salt and water) formation in crucibles and/or possible corrosion reactions with crucibles.

Heat Capacity of $NaCl-MgCl_2-UCl_3$ System

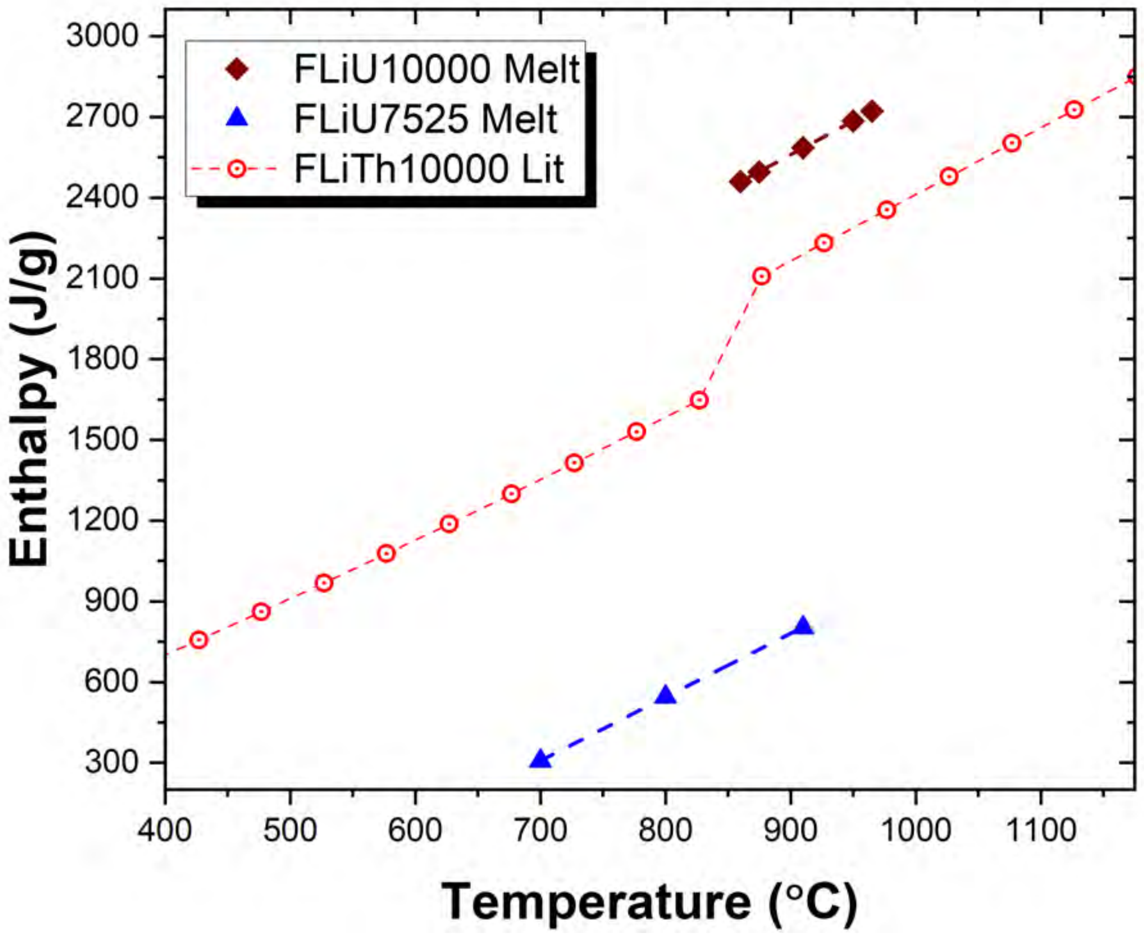
$\Delta H, C_p$



- Heat capacity of melt measured from 600 to 1000°C using TCDC.
  - ClNaMg5842 decreases from 1.1615 J/g·K at 600°C to 1.0615 J/g·K by 1000°C.
- Results compare well with NIST-JANAF tables.
  - ~6% error at liquid state.
    - A fraction of the drops performed so far as NaCl-KCl series increasing total error.
- It appears that the extra energies found in the enthalpy signals are invariant with temperature above melt.
  - i.e. They don't have large effects on the slope of the curves used for heat capacity calculations.

Enthalpy of the LiF-UF4 System

$\Delta H, C_p$



- Experimental values for LiF range from ~3460 J/g at 875°C and increase to 2722 J/g at 965°C.
- Enthalpy increases with temperature for all compositions.
- Melt measurements are closer to NIST JANAF literature than Cl salts.
  - ➢ Could be due to less hygroscopic nature of F salts.
- Significant gap in values between pure LiF and LiF-ThU_4 eutectic.
  - ➢ Generally lighter atomic mass of cation leads to higher phonon frequencies and higher enthalpy.
  - ➢ This is atomic mass gap is greatly enhanced when actinide element is added.

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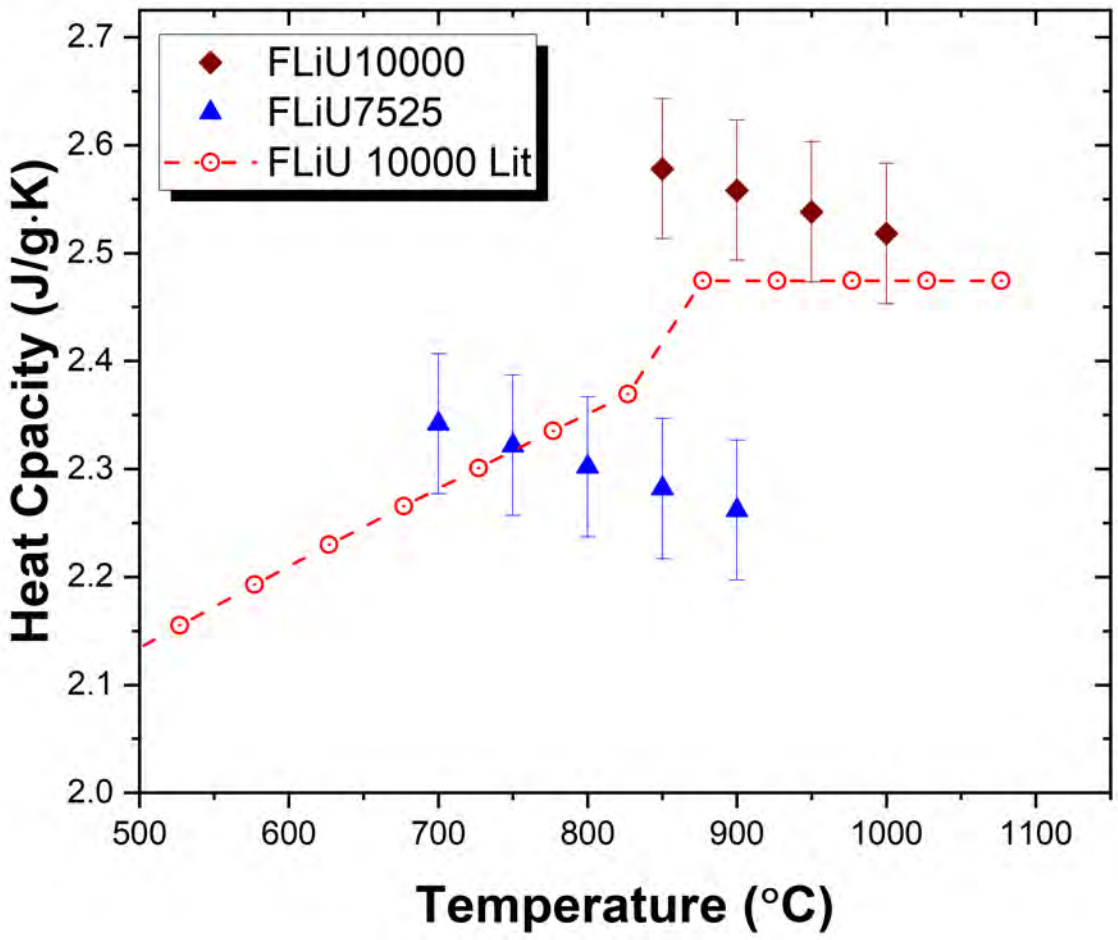
Heat Capacity of the LiF-UF4 System

$\Delta H, C_p$

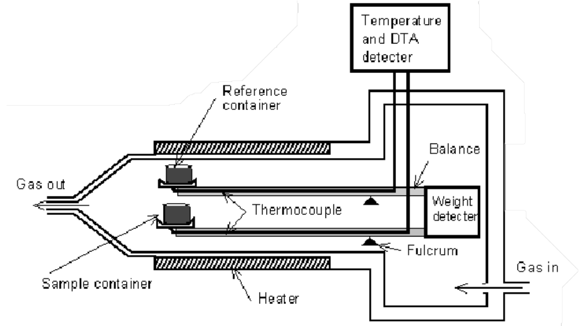


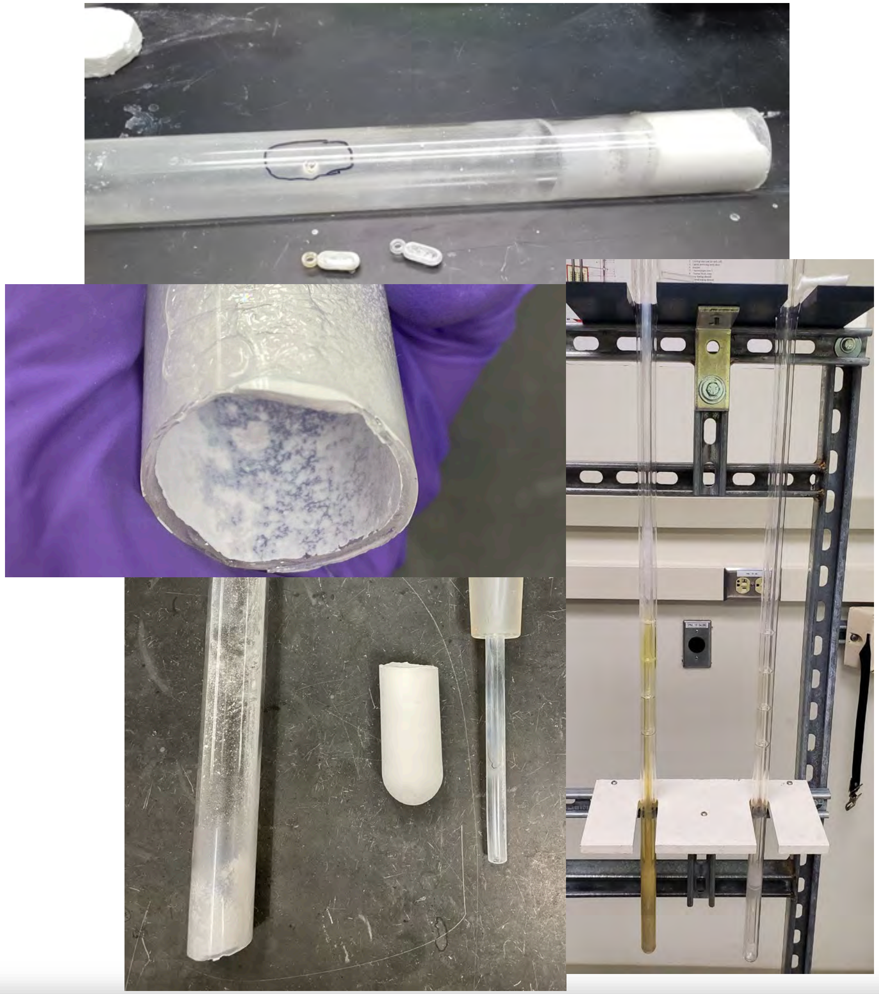
- Heat capacity of melt measured from 700 to 1000°C using TCDC.
  - FLiU 7525 decreases from 2.342 J/g·K at 700°C to 2.262 J/g·K by 1000°C.
- Results compare well with NIST-JANAF tables.
  - ~6% error at liquid state.
- Effect of atomic mass on heat capacity appears to track with enthalpy.
  - i.e. heavier atomic mass leads to lower phonon frequencies and reduced heat capacity.
- Reactor design will require balancing fuel load and desired heat capacity.
  - Will actinide additions lead to detrimental effects on other thermal properties?

Thermal Stability
(Volatility & Vapor Pressure)

$p^*, \Delta H_v$

- Homogenization work identified evaporation of NaCl-KCl salts at ambient pressures.
  - Mass loss detected with flowing Ar or Air.
  - Future work with actinides.
  - Will fission products separate from parent salt?
- Currently running TGA-DTA & RGA-MS experiments to track weight loss vs time vs temp.





TGA: Measures weight change in relation to temperature change.

Experimental Parameters (TGA)

- Temperatures from 400 to 900 °C
- Quick ramp to temp and hold.
- Flow: Breathing Ar 10 mL/min

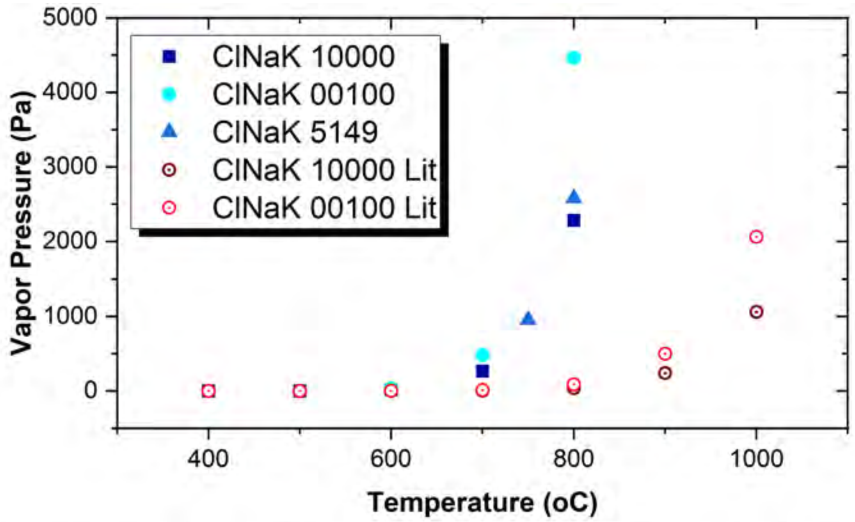
Vapor Pressure (TGA)

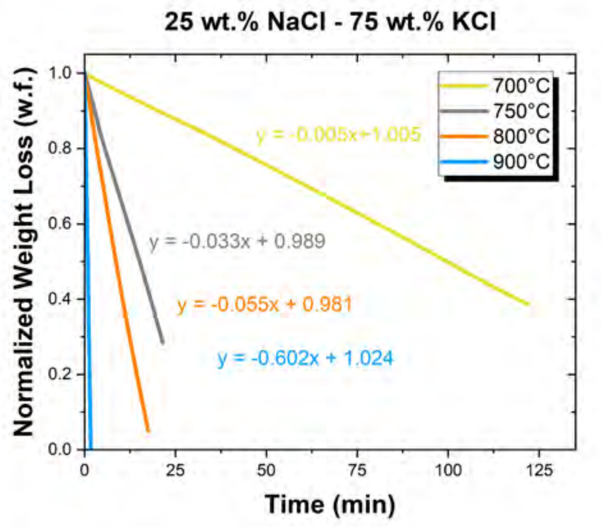
$p^*, \Delta H_v$

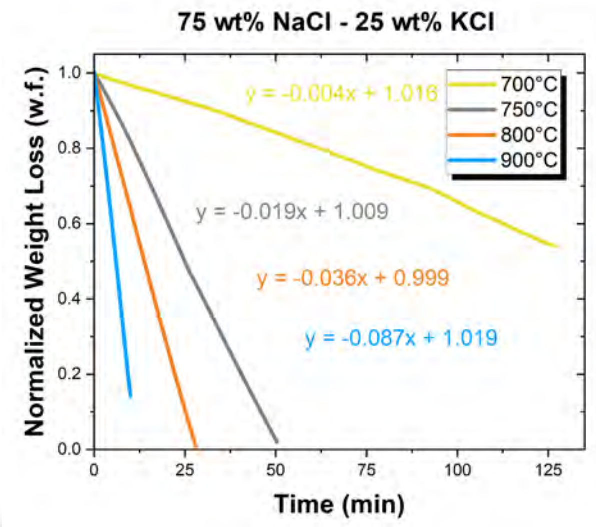
Langmuir Equation's:

$$p = k\upsilon \qquad k = \frac{\sqrt{2\pi R}}{\alpha} \qquad v = \left(\frac{1}{a}\right)\left(\frac{dm}{dt}\right)\sqrt{\frac{T}{M}}$$

- Experimental data significantly different than values found in NIST JANAF database.
  - ➢ Is this discrepancy due to impurities or water content?
    - o Little data available on the effect of H_2O or O-H bonds on thermal stability.
  - ➢ Could the assumption of little to no volatility from melt to boiling point be incorrect?
    - o NIST JANAF data on NaCl & KCl is comprised of two papers from 1926 and 1954.
    - o There is a need to confirm and validate data with modern methods and instrumentation.







Enthalpy of Volatility and Sublimation

$p^*, \Delta H_v$

Antoine Equation

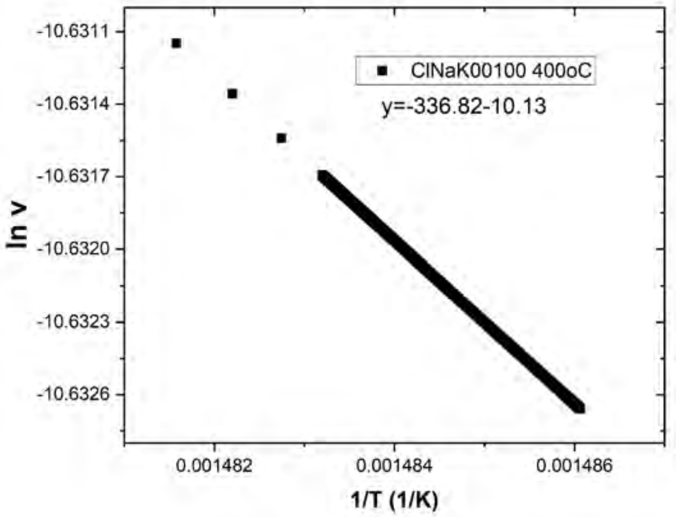
$$\ln v = A - \frac{\Delta H}{RT}$$

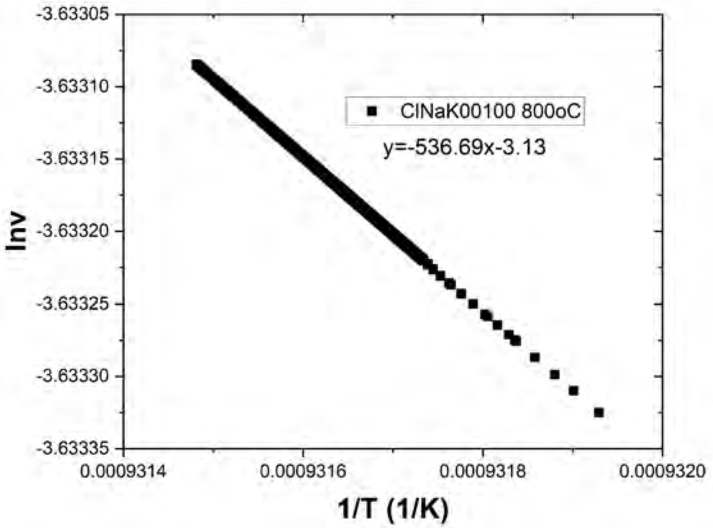
- The Antoine equation allows us to calculate enthalpy of volatility and sublimation.
- These calculations will allow us to correct the overestimation of enthalpy from the drop calorimeter.

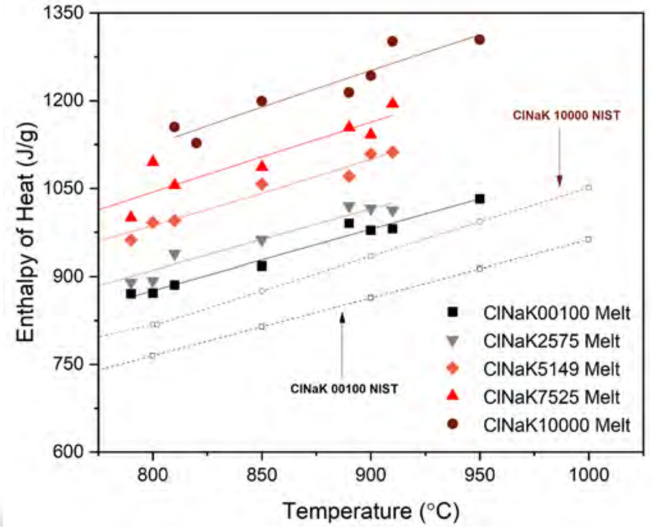
	ClNaK00100	ClNaK10000	H2O
Enthalpy of Volatility (J/g)	4462	4987	2256
Enthalpy of Sublimation (J/g)	2430	2800	2836

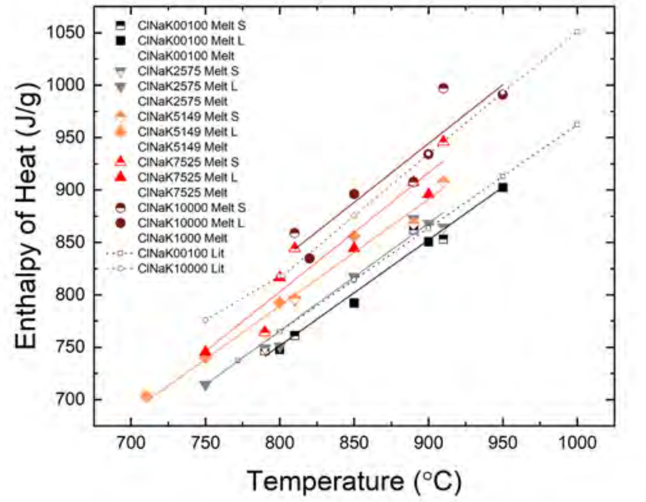
$$\Delta H_{ds} = \Delta H_{hc} + \Delta H_{ph} + \Delta H_{rxn}$$

- Estimated vapor phase in drop calorimetry crucibles
  - ➢ CLNaK00100: ~2 wt%
  - ➢ CLNaK10000: ~4 wt%









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Residual gas analysis mass spectrometry (RGA-MS)

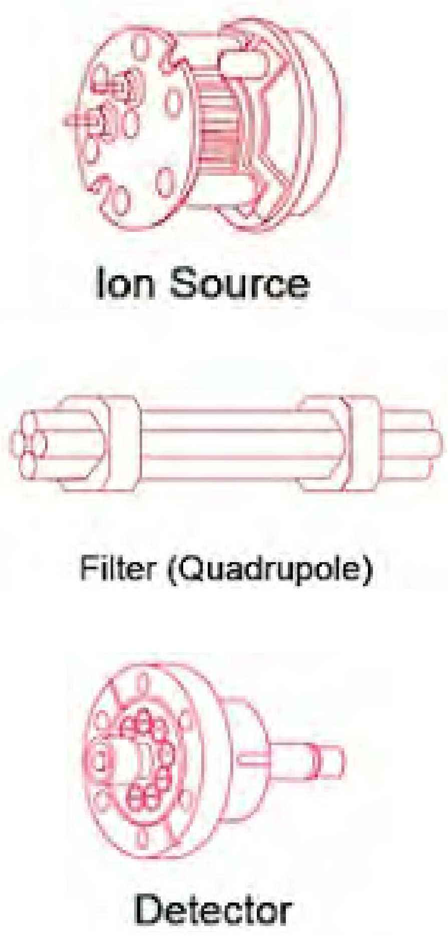
$p^*, \Delta H_v$

Mass Spectrometry

- Determines chemical components within the off-gas a material emits
- Gas is taken through the ion source to become ionized and flow through the quadrupole
- The quadrupole consists of cylindrical rods that act as electrodes both positively and negatively charged to accelerate the ions
- Detection limit of 200 atomic mass units

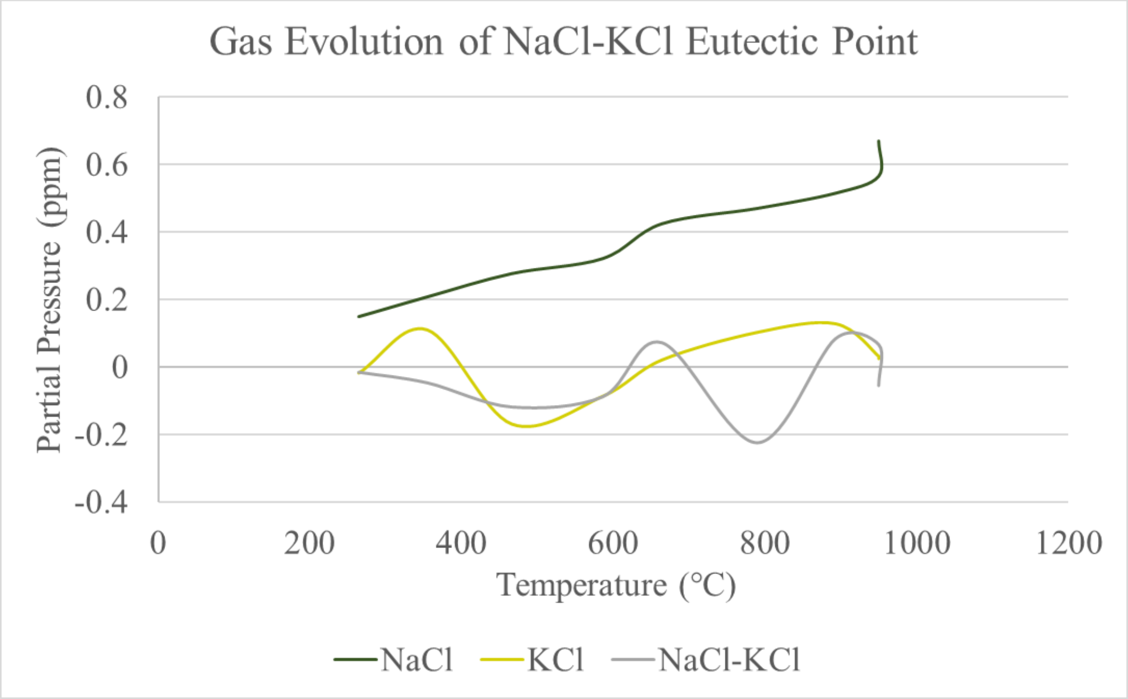
Experimental Parameters (RGA-MS)

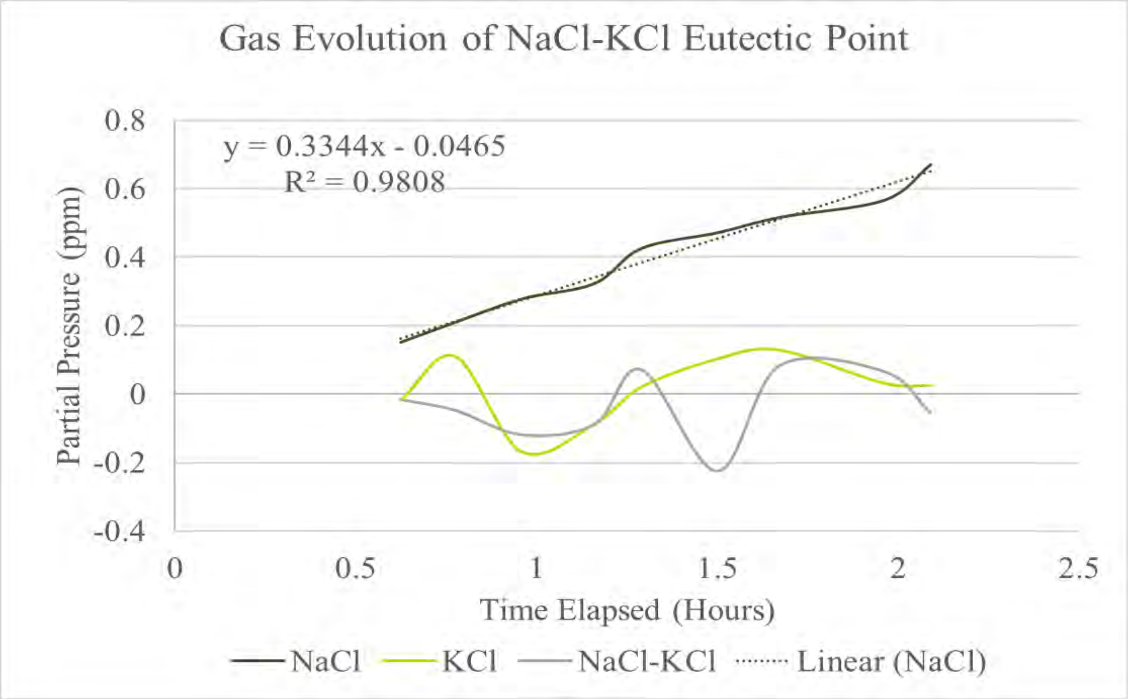
- Temperatures from 200 to 1000 °C
- Flow: Breathing Ar 10 mL/min
- Salts melted in Quartz tube
- Argon over gas with a flow rate of 50 mL/min.
- Capillary line attached to furnace and the RGA was held at 200°C to reduce salt condensation.



Residual gas analysis mass spectrometry (RGA-MS)

$p^*, \Delta H_v$

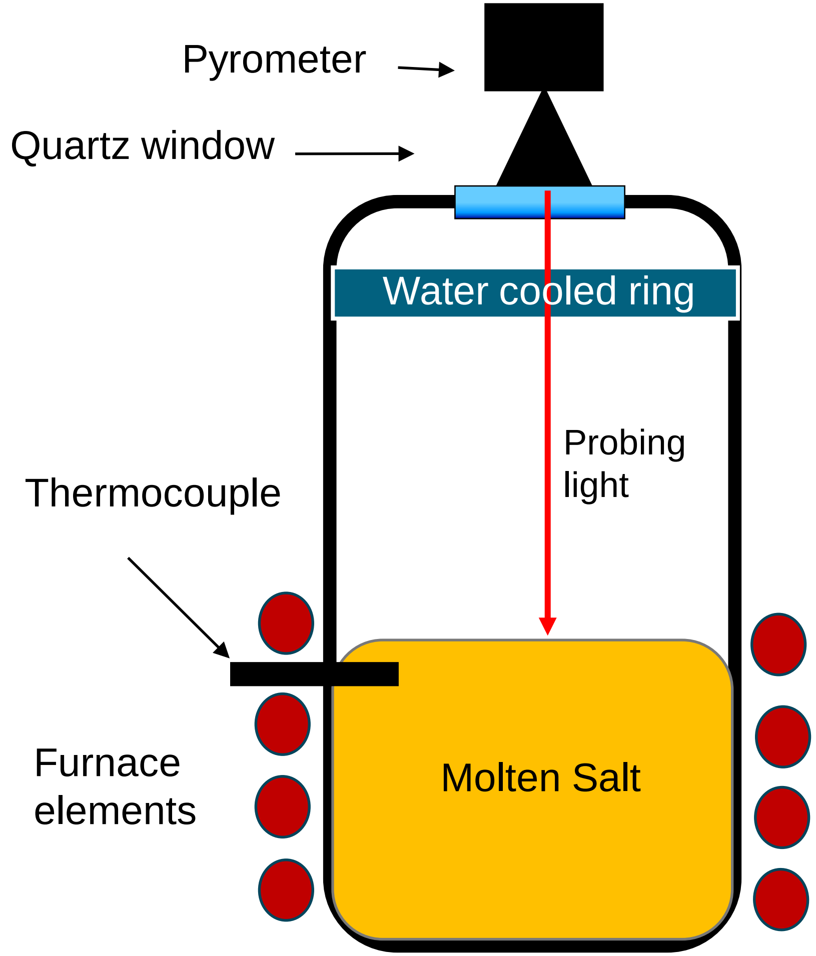




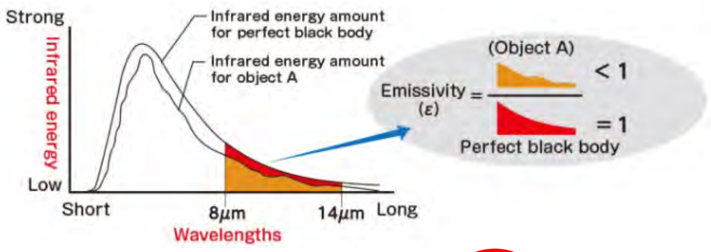
- NaCl is vaporizing before melting point
- NaCl is leaving the system while KCl does not show evidence of vaporizing

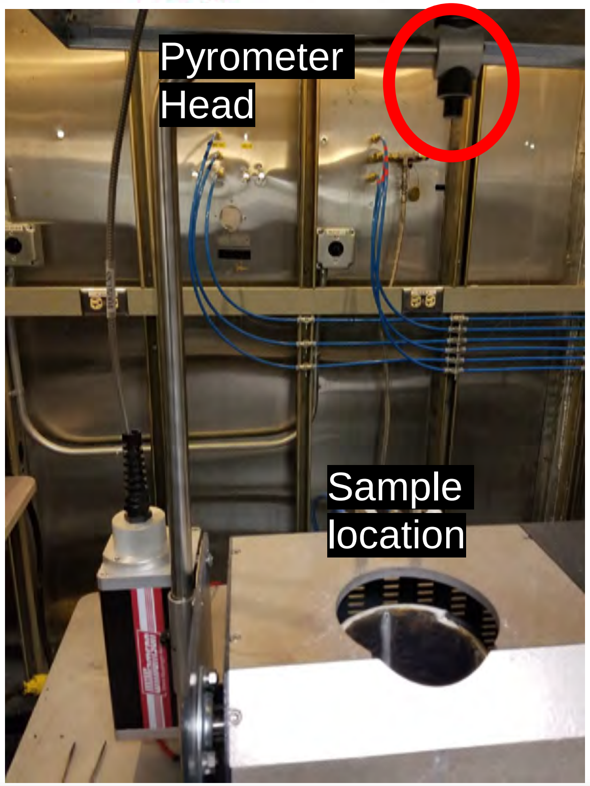
- Starting composition has changed throughout thermal experiments
- Thermal properties will need a volatilization correction factor based on results

Emissivity Measurements



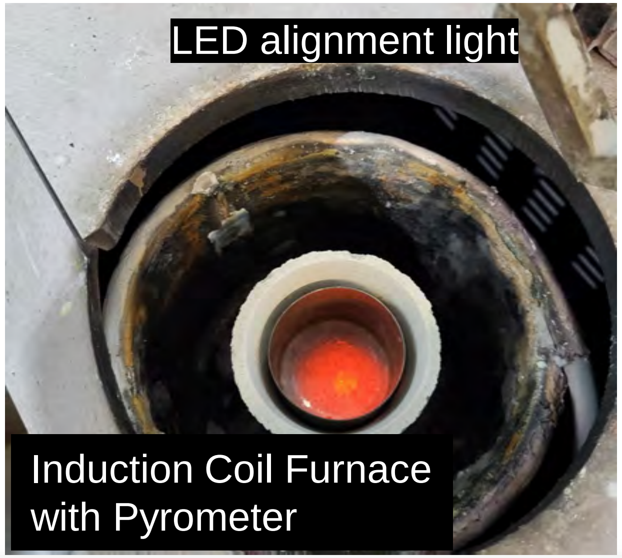
$$j^* = \varepsilon \sigma T^4$$



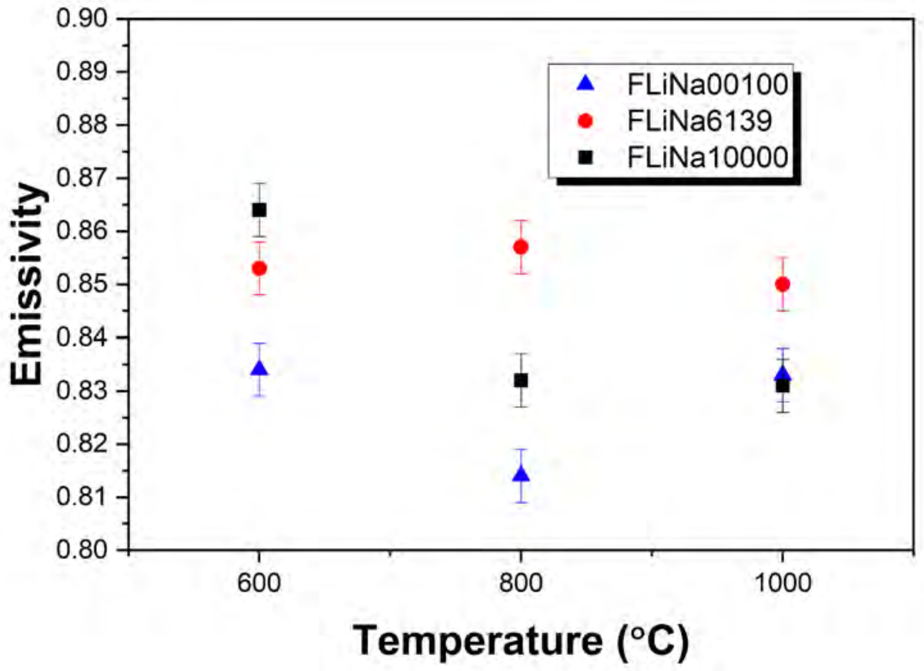


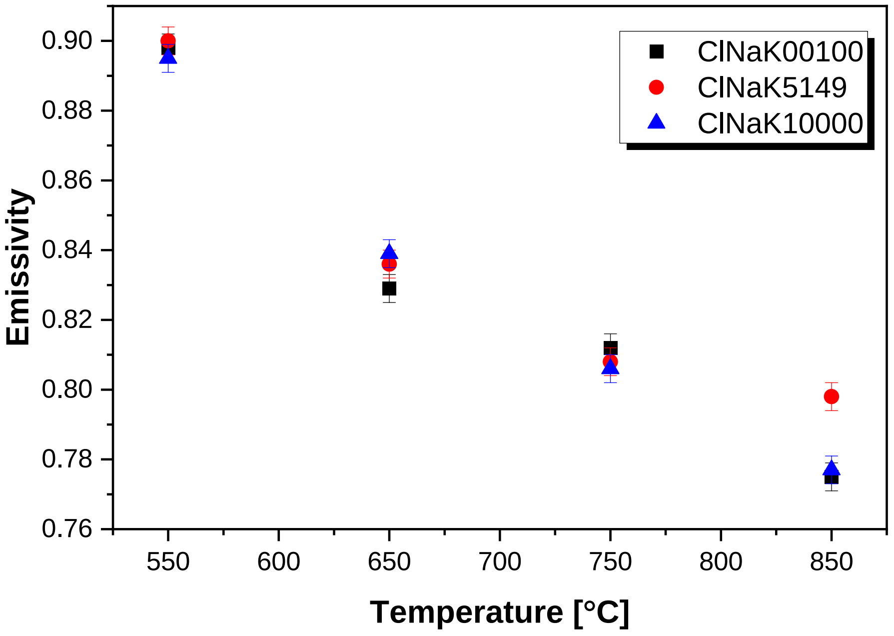
Measurement Technique

1. Measure temperature of salt with pyrometer (ideally in a sealed system).
2. Measure the temperature of salt or air space directly above salt with a calibrated thermometer.
3. Adjust emissivity value on pyrometer until temperature reading matches thermocouple.



Emissivity (NaCl-KCl & LiF-NaF)



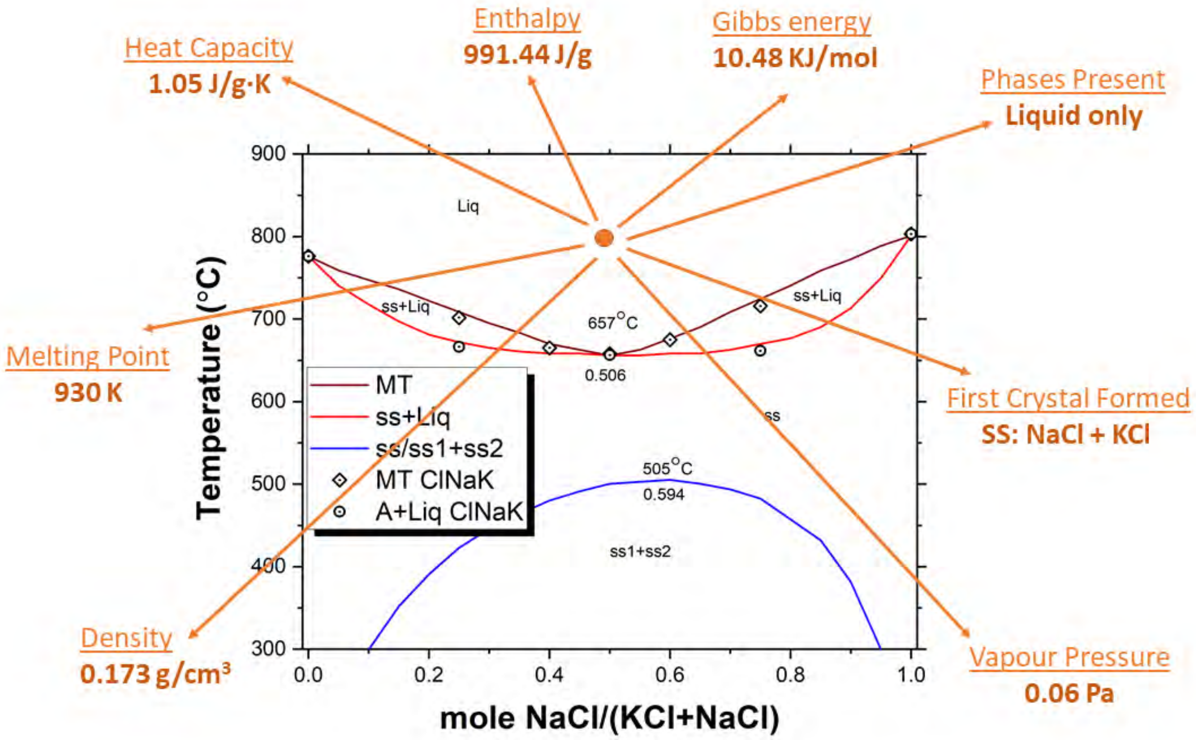


- Both Cl and F Salts exhibit a decrease in emissivity with increasing temperature.
- Emissivity's measured between 0.77 and 0.90.
  - Relatively high emissivity could imply high radiative absorption and heat transfer.
- Fluoride salts exhibit higher emissivity at a given temperature that chloride salts
  - Higher bond energy means more light is absorbed and emitted.

Compound	D^{o}_{298} (KJ/mol)
NaCl	412.1
KCl	433
LiF	577
NaF	477.3

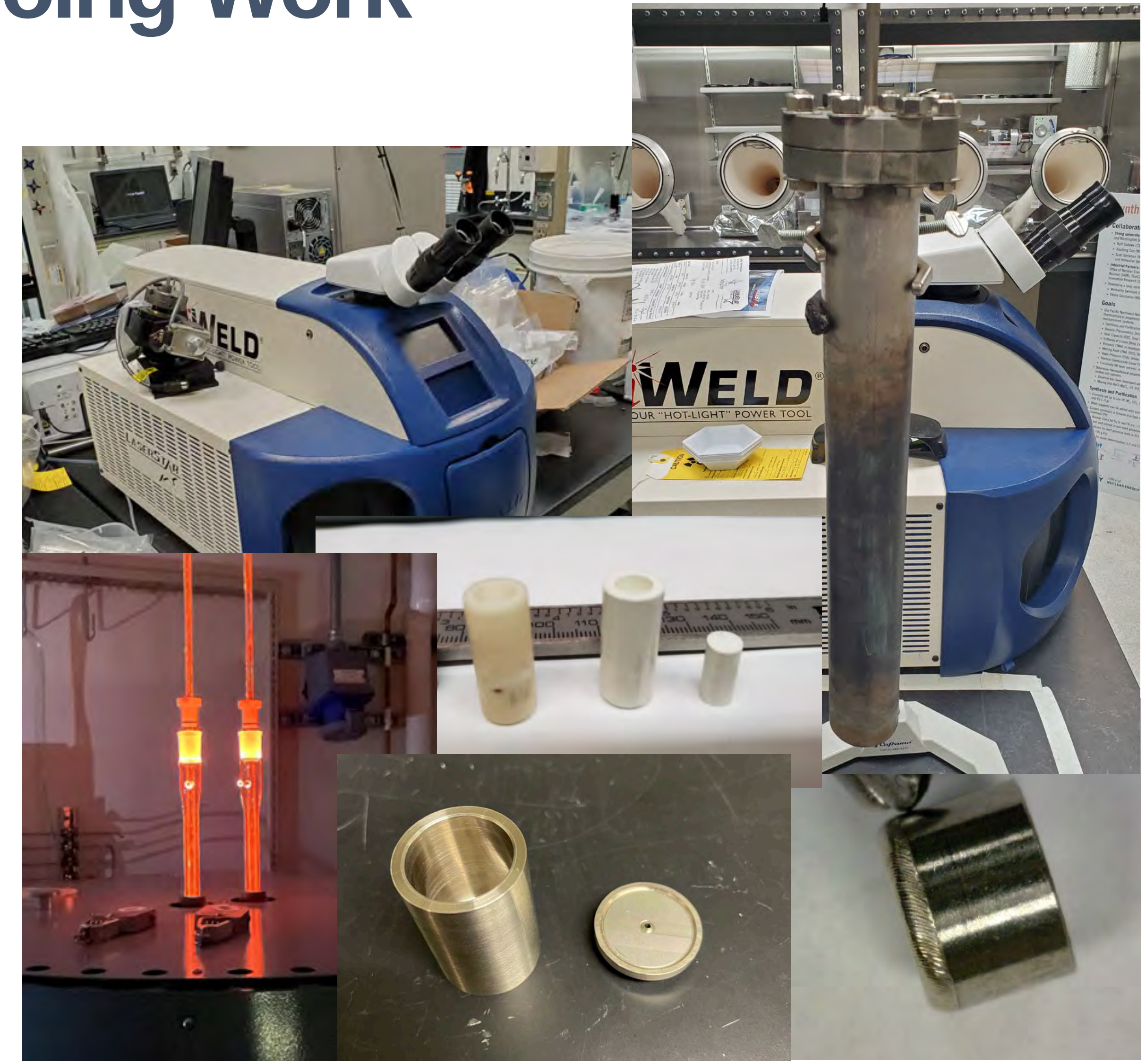
Summary

- A system of eight thermophysical properties have been identified as important for the design of a MSR reactor.
  - ρ, η, C_p,ΔH, m.p., p*, α, ε
  - Six of the eight properties have reportable data.
- Unpurified F & Cl powders exhibited no detectible impurities (XRD) and no mass loss in the DTA at temperatures below 400°C.
  - DTA-TGA has determined vapor pressures significantly higher than NIST-JANAF reported values above 600°C.
- Two methods of pycnometry based liquid density measurement have been developed.
  - Initial measurements are in good agreement with literature
  - Scalable to less than 100mg of salt.
- DSC and HTDC data is complete on a full set of ClNaK and preliminary ClNaMg, ClNaU, FLiU compositions.
  - ΔH and C_p values are consistent with previously reported on both F and Cl salts.
- Emissivity measurement system has been developed.
  - Initial measurements on FLiNa and ClNaK systems.



Future & Ongoing Work

- Continue development of density, viscosity, vapor pressure and thermal diffusivity measurement capabilities.
  - Install density and vapor pressure equipment into radiological spaces.
  - Develop improved methods for high volatility salts.
- Publish thermophysical data on NaCl-KCl system.
  - "Thermodynamic Investigation of the NaCl-KCl Salt System from 25 to 950 °C", **J. Lonergan**, V. Goncharov, M. Swinhart, K. Makovsky, M. Rollog, B. McNamara, R. Clark, D. Cutforth, C. Armstrong, X. Guo, P. Paviet, *Journal of Molecular Liquids*, 2023, (**under review**).
- Continue investigating LiF-NaF-UF_4, and NaCl-MgCl2-UCl_3 systems.
- Continue development of AIMD models to supplement microstructure and physical property characterization.
- Start synthesis, purification, and testing of UCl_3 and UF_4 produced in house.
- Start systematic investigation on the effects of water content and impurities (Ni, Fe, Cr,…) on thermophysical properties.



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UCl_3 & NaCl-$MgCl_2$ Salts: TerraPower

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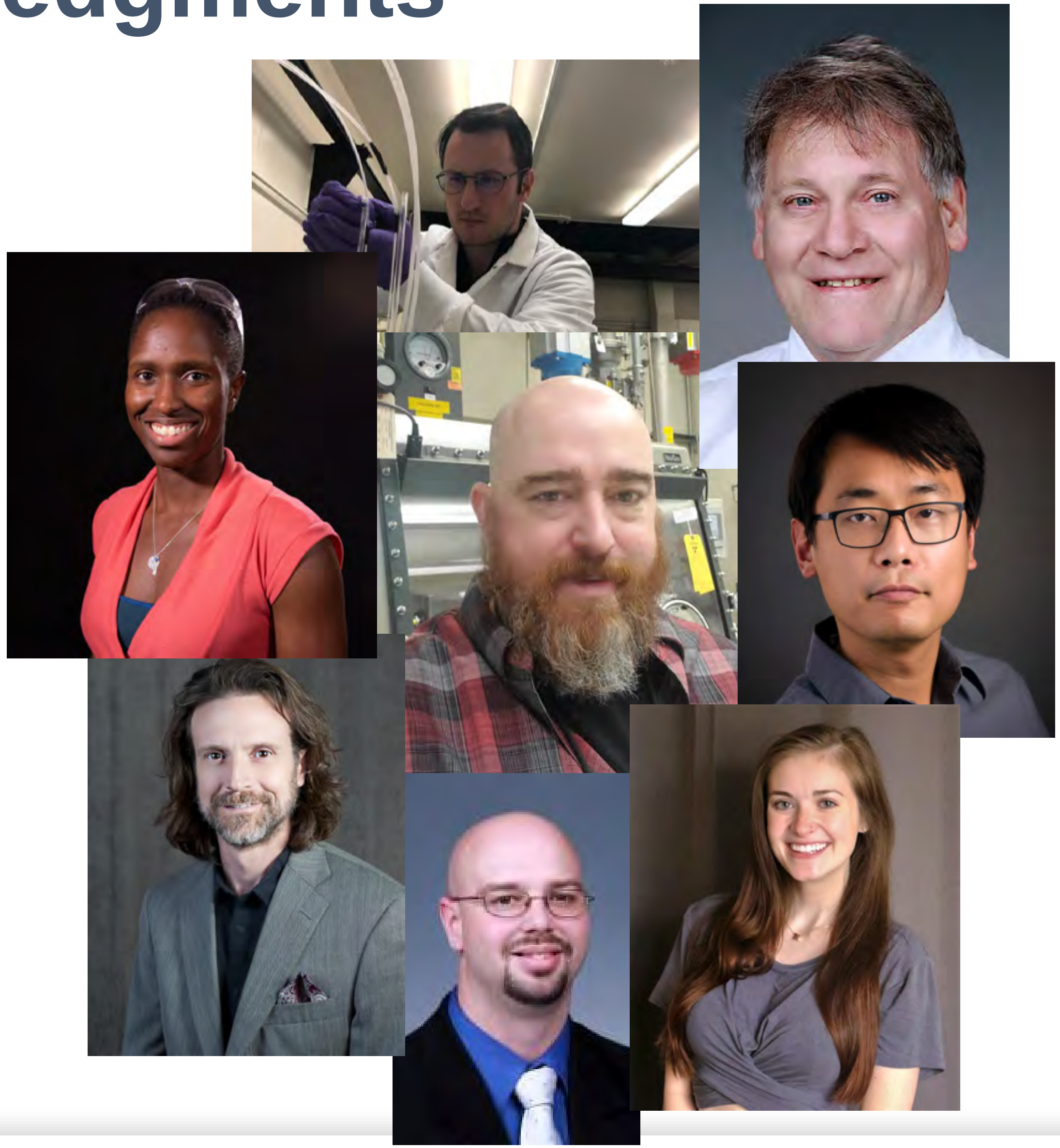

Thank you !!

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