INL/CON-23-71703-Revision-1

TMS 2023 - Methodology and Density of PuCl3-NaCl Mixtures

March 2023

Changing the World's Energy Future

Michael Ellis Woods, Toni Y Karlsson, Ruchi Gakhar

Idaho National Laboratory

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Idaho Falls, Idaho 83415

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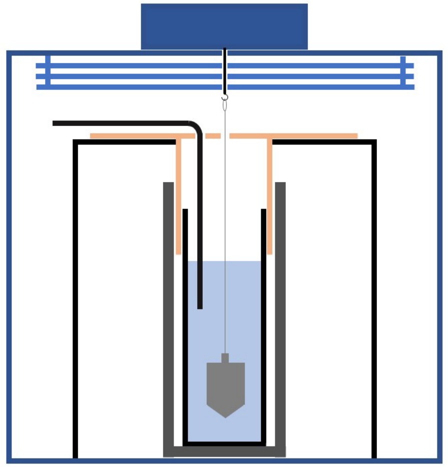
March 20th, 2023

***Michael Woods*, Toni Karlsson, Ruchi Gakhar**

Advanced Technology of Molten Salts



Methodology and Density of PuCl3-NaCl Mixtures

INL/CON-23-71703

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Idaho National Laboratory

Motivation and research team

- High fidelity density data of chloride salts needed for MSR modelling efforts
- Lack of available literature data and modern setups
- **What did we do?**
- Created a setup for this measurement (hydrostatic buoyancy method)
- $PuCl_3$-NaCl mixture (36 mol% $PuCl_3$) prepared by chlorination of Pu metal by NH_4Cl
- Density of 36 mol% and 25 mol% $PuCl_3$ measured
- Analysis of minor contributing factors and individual experimental errors
- "Synthesis and Thermophysical Property Determination of NaCl-$PuCl_3$ Salts" Karlsson et al. *J. Mol. Liq*. (2023) Accepted.

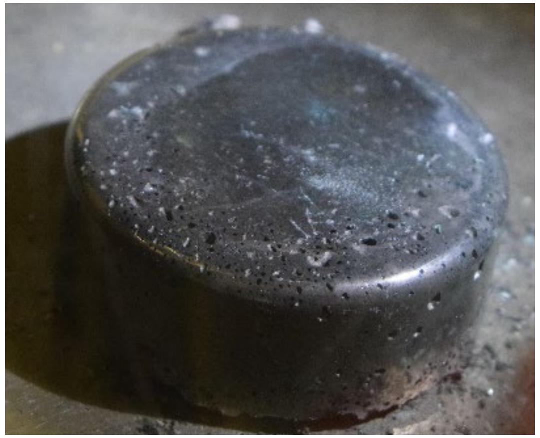
Michael Woods

Toni Karlsson

Ruchi Gakhar

Synthesis of PuCl3-NaCl

- Preparation of the Pu metal
- Pu metal reacted with hydrogen (hydride)
  - $Pu + H_2 \longrightarrow PuH_3$
- Then heated under vacuum (dehydride)
  - $PuH_3 \longrightarrow Pu + H_2$
- Pu mixed with NH_4Cl and NaCl
- Slow heating rate to temper the exothermic reaction



$$\boldsymbol{Pu_{(s)} + 3NH_4Cl_{(s)} \rightarrow PuCl_{3\,(s)} + 3NH_{3\,(g)} + 1.5H_{2\,(g)}} \quad \textbf{(1)}$$

$$NH_4Cl\ _{(s)} \rightarrow NH_{3\,(g)} + HCl_{(g)} \quad (2)$$

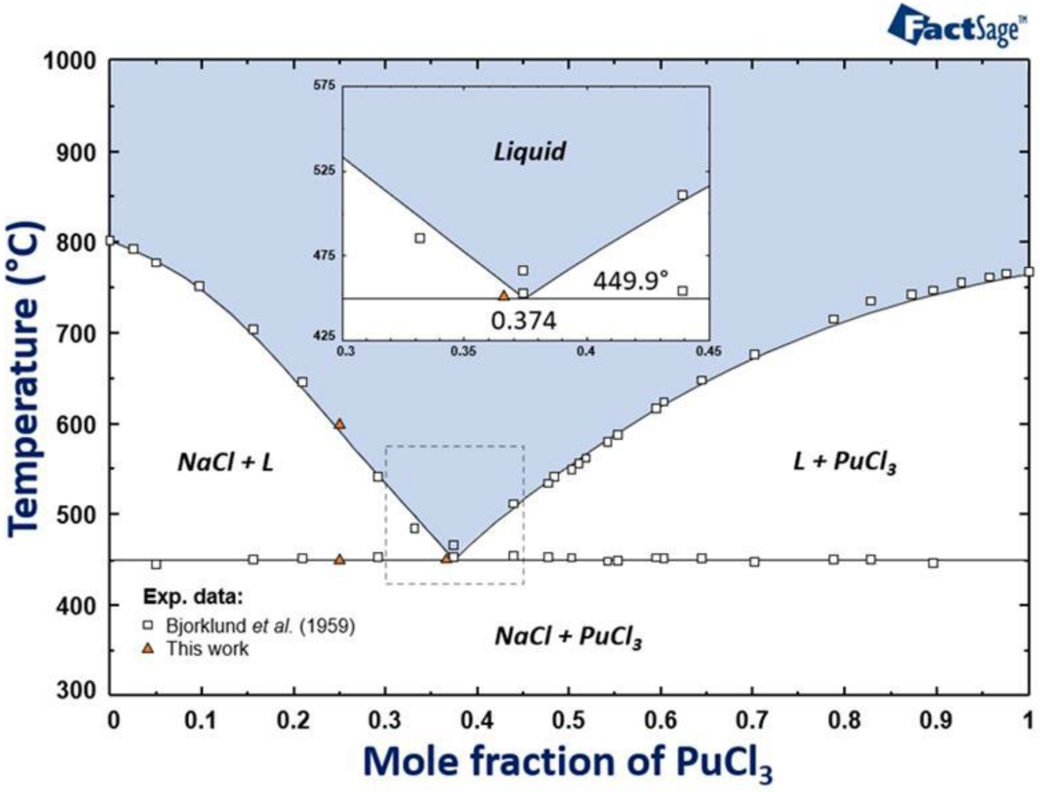
$$Pu_{(s)} + \ 3HCl_{(g)} \rightleftharpoons PuCl_{3\,(s)} + \ 1.5H_{2\,(g)} \quad (3)$$

$$\boldsymbol{Pu_{(s)} + 3NH_4Cl_{(s)} + NaCl_{(s)} \rightarrow PuCl_{3\,(s)} + \ NaCl_{(s)} + \ 3NH_{3\,(g)} + 1.5H_{2\,(g)}} \textbf{(4)}$$

CRADA No. 18-CR-17, "Integrated Effects Testing for a Molten Chloride Fast Reactor."

Synthesis of PuCl3-NaCl

- Prepared as eutectic 36 mol% $PuCl_3$
- Elemental analysis and gamma spectroscopy
  - 63.3 mol% NaCl (22.6 wt%)
  - 36.2 mol% $PuCl_3$ (76.4 wt%)
  - 0.5 mol% other (1.05 wt%)
    - $FeCl_3$, UCl_3, $NpCl_3$, $AmCl_3$
- Salt purity is 99.5%
- Density measurements at 36 mol% $PuCl_3$
  - Added NaCl to achieve 25 mol% $PuCl_3$



Schorne-Pinto, J., et al., *Correlational Approach to Predict the Enthalpy of Mixing for Chloride Melt Systems.* ACS Omega, 2022. **7**(1): p. 362-371.

High temperature liquid density

- **Archimedes hydrostatic method**

$$\rho_{liquid} = \frac{M_{air} - W_{liquid}}{\Delta V}$$

J. Chem. Eng. Data **2001**, 46, 1203−1205

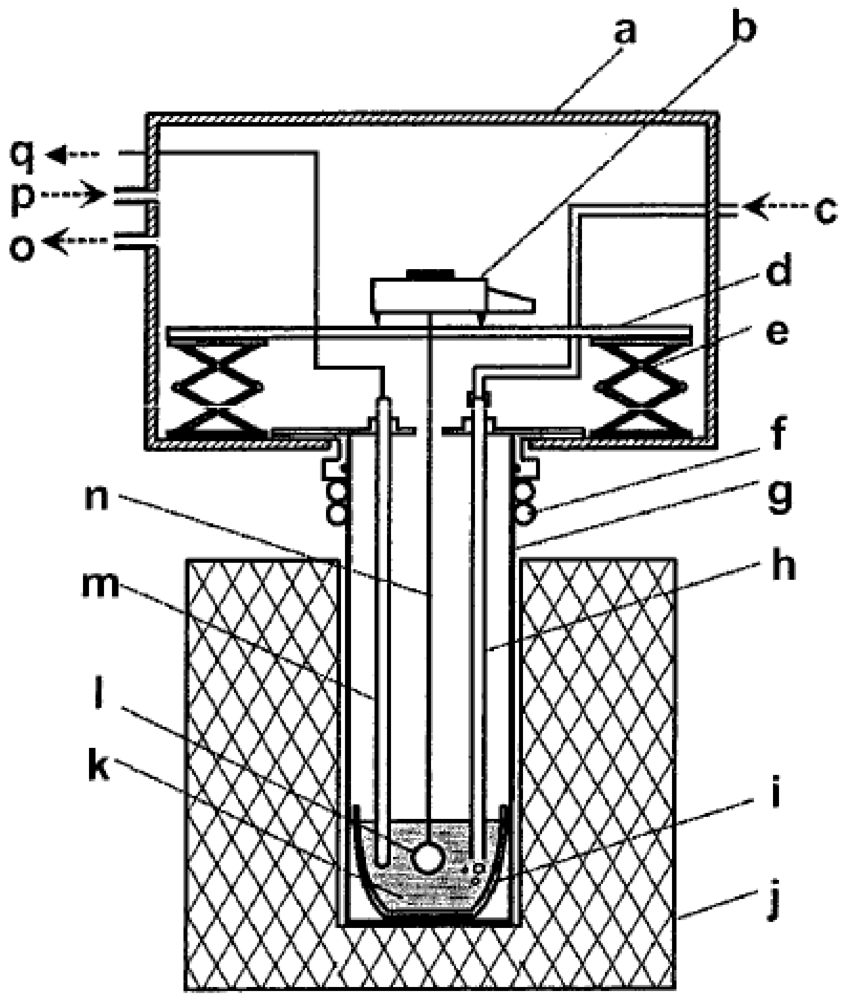
Densities of Eutectic Mixtures of Molten Alkali Chlorides below 673 K

Hiroshi Ito* and Yasuo Hasegawa

Mechanical Engineering Laboratory, AIST, METI, 1-2 Namiki Tsukuba 305-8564, Japan

Yasuhiko Ito

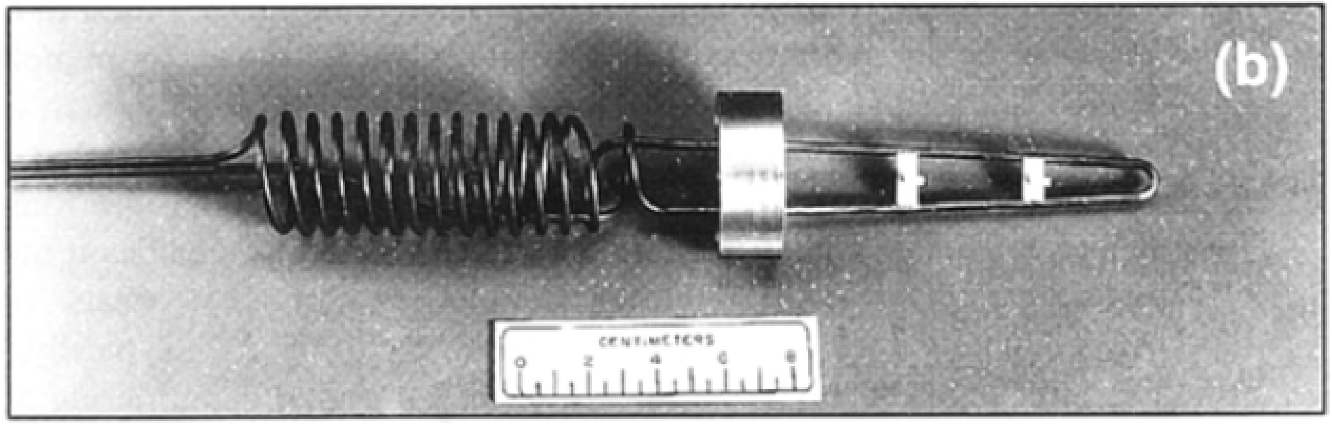
Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Kyoto 606-8501, Japan



High temperature liquid density

- **Vibrating U-tube densimeter**

$$\rho - \rho_0 = \kappa(\tau^2 - \tau_0^2)$$



International Journal of Thermophysics, Vol. 17, No. 1, 1996

A Vibrating-Tube Densimeter for Fluids at High Pressures and Temperatures[1]

J. G. Blencoe,[2,3] S. E. Drummond,[2] J. C. Seitz,[2] and B. E. Nesbitt[4]

High temperature liquid density

- **Maximum bubble pressure**

$$P = (\rho_{liquid} - \rho_{gas})gx + \frac{2\gamma}{r}$$

Journal of Industrial and Engineering Chemistry 63 (2018) 149–156

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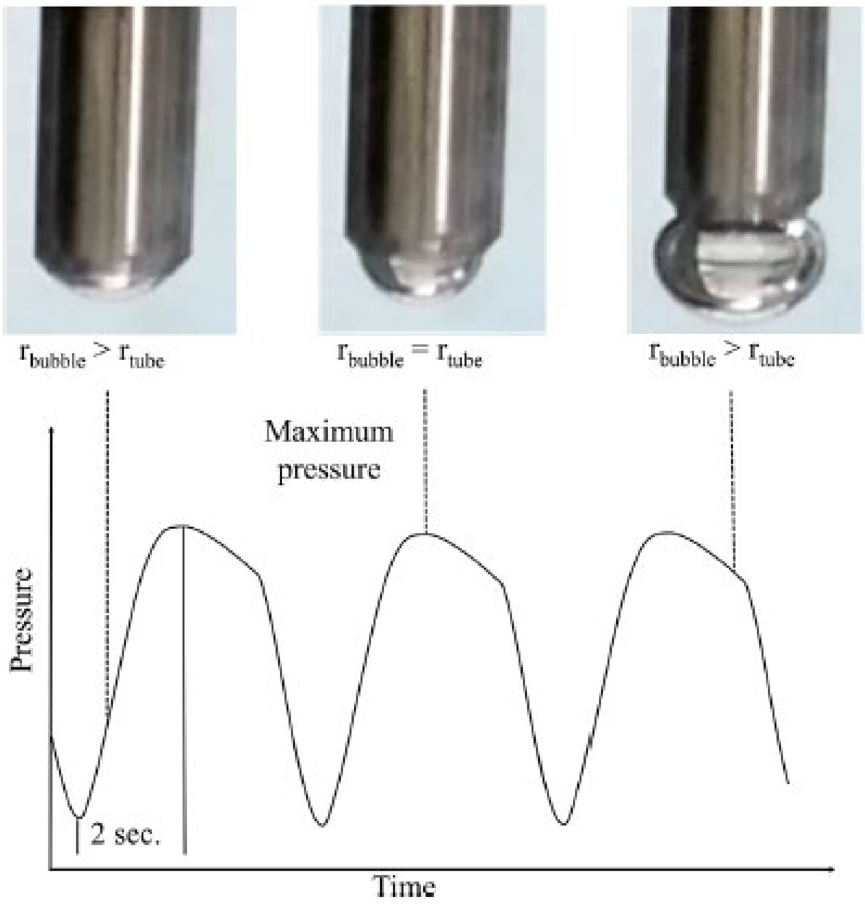
journal homepage: www.elsevier.com/locate/jiec

Accurate determination of density, surface tension, and vessel depth using a triple bubbler system☆

Ammon N. Williams*, Greg G. Galbreth, Jeff Sanders

Idaho National Laboratory, 2525 Fremont Ave, Idaho Falls, ID, 83401, United States

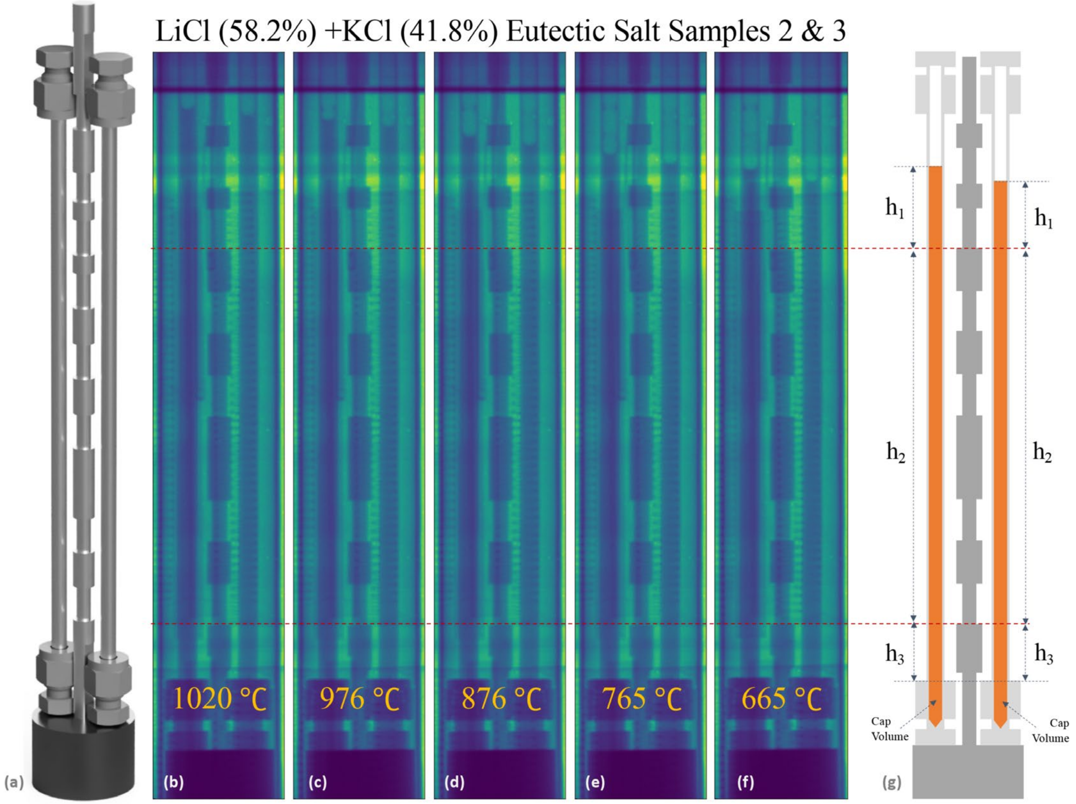


High temperature liquid density

- Other
  - Dilatometry
  - Hydrometer
  - Pycnometry

Krome Dispense. Triple Scale Hydrometer – No lead and Mercury - Krome Dispense

Thermcraft. TransTemp (thermcraftinc.com)




Journal of Imaging
MDPI

Article

Remote Density Measurements of Molten Salts via Neutron Radiography

Alexander M. Long [1,*], S. Scott Parker [1], D. Travis Carver [1], J. Matt Jackson [1], Marisa J. Monreal [2], Darcy A. Newmark [3] and Sven C. Vogel [1]

High temperature liquid density

- **Archimedes hydrostatic method**

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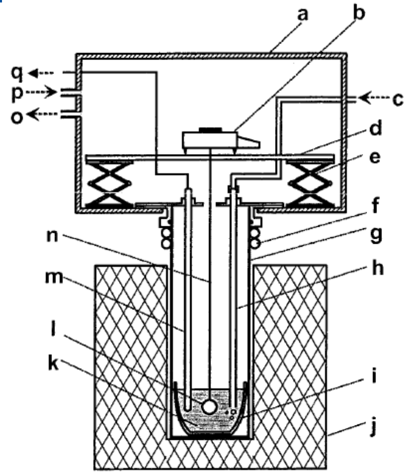
Densities of Eutectic Mixtures of Molten Alkali Chlorides below 673 K

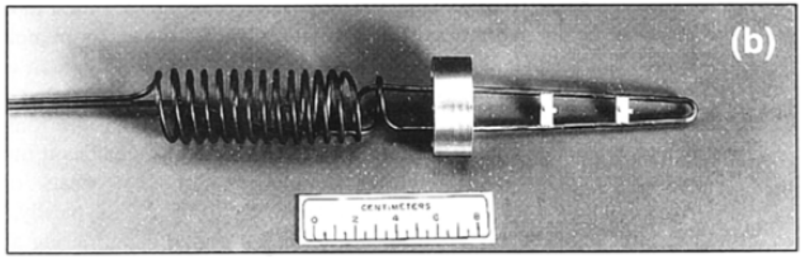
Hiroshi Ito* and Yasuo Hasegawa
Mechanical Engineering Laboratory, AIST, METI, 1-2 Namiki Tsukuba 305-8564, Japan
Yasuhiko Ito
Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Kyoto 606-8501, Japan

$$\rho_{liquid} = \frac{M_{air} - W_{liquid}}{\Delta V}$$



- **Vibrating U-tube densimeter**

International Journal of Thermophysics, Vol. 17, No. 1, 1996



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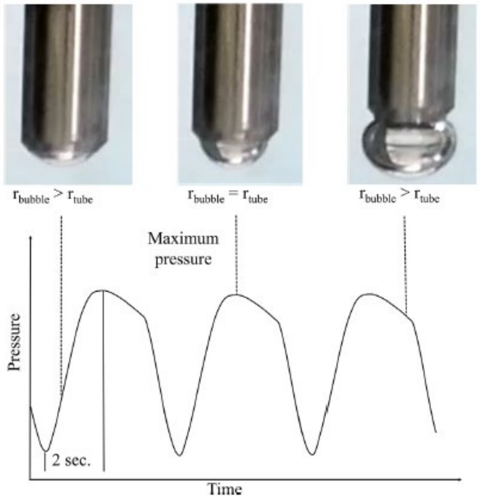
$$\rho - \rho_0 = \kappa(\tau^2 - \tau_0^2)$$

- **Maximum bubble pressure**



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Accurate determination of density, surface tension, and vessel depth using a triple bubbler system☆

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$$P = (\rho_{liquid} - \rho_{gas})gx + \frac{2\gamma}{r}$$

- **Other**
  - Dilatometry
  - Hydrometer
  - Pycnometer

Journal of Imaging
MDPI
Article

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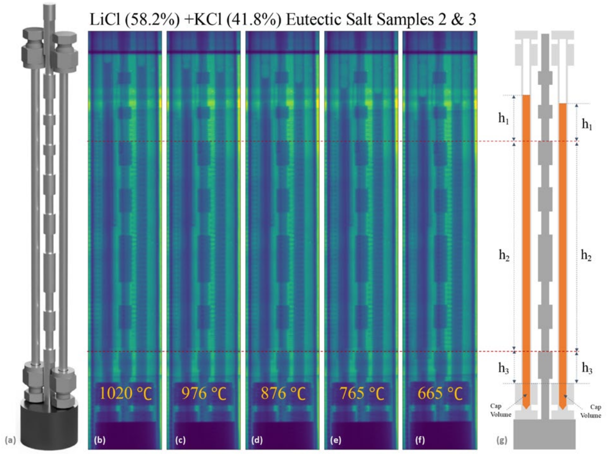
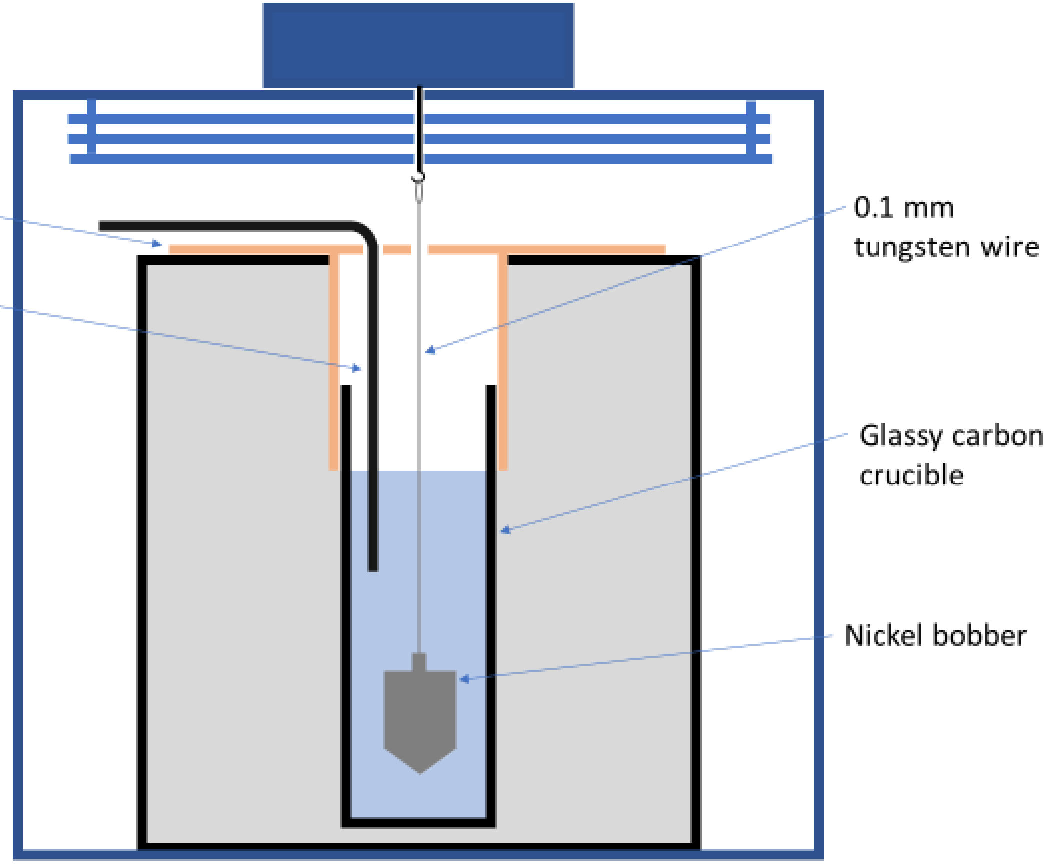
Alexander M. Long [1,*], S. Scott Parker [1], D. Travis Carver [1], J. Matt Jackson [1], Marisa J. Monreal [2], Darcy A. Newmark [3] and Sven C. Vogel [1]



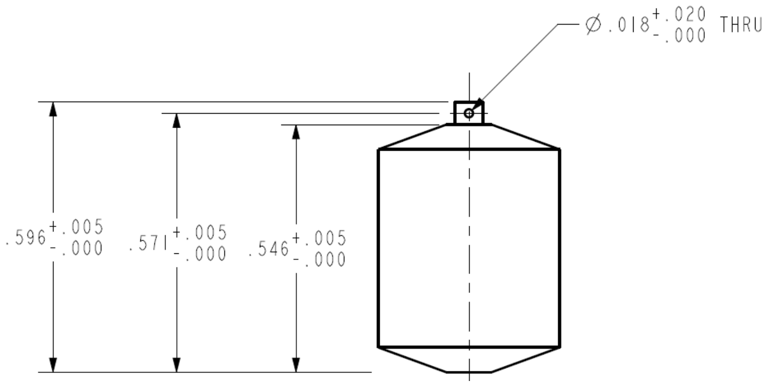
Density of $PuCl_3$-NaCl mixtures



- Archimedes hydrostatic method

$$\rho_{salt} = \frac{M_{air} - W_{salt} + \frac{\pi D \gamma}{g}}{V_0[1 + \propto (T - T_0)]^3}$$

- 10 mL liquid sample, 1 cm^3 bobber
- V_0 measured in DI water and ethanol
- 5 mass measurements per temperature



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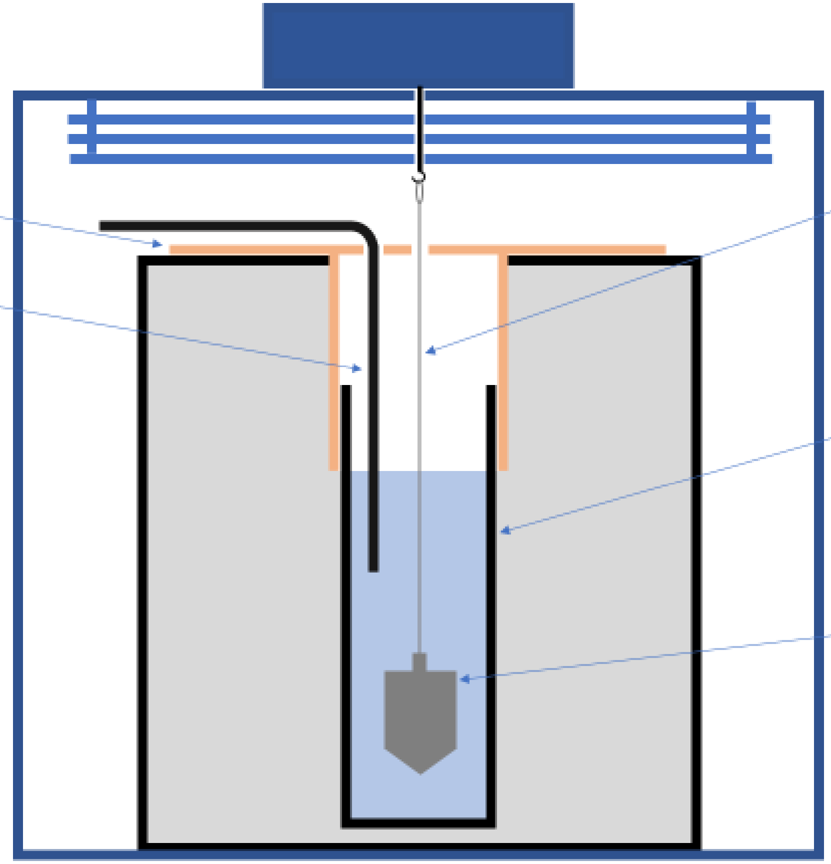
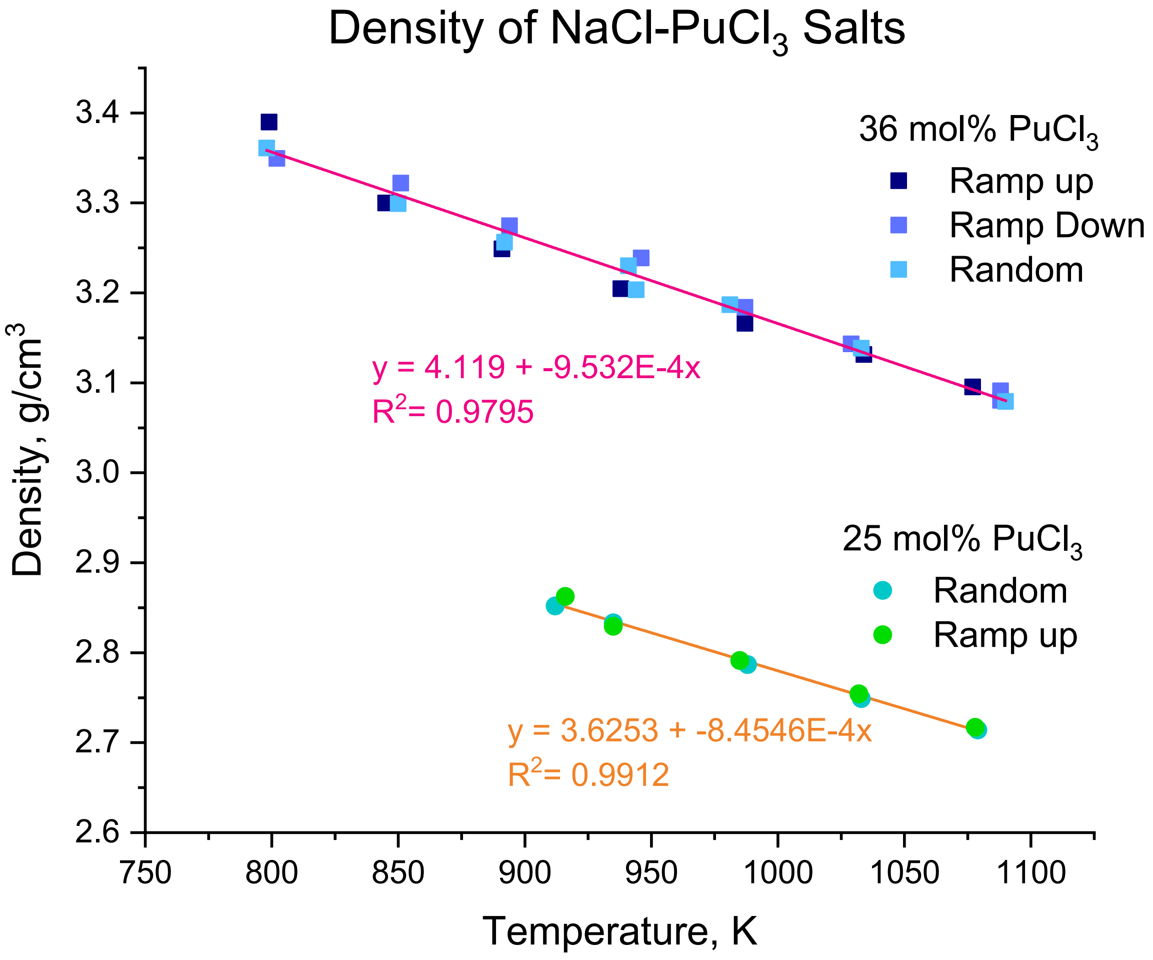


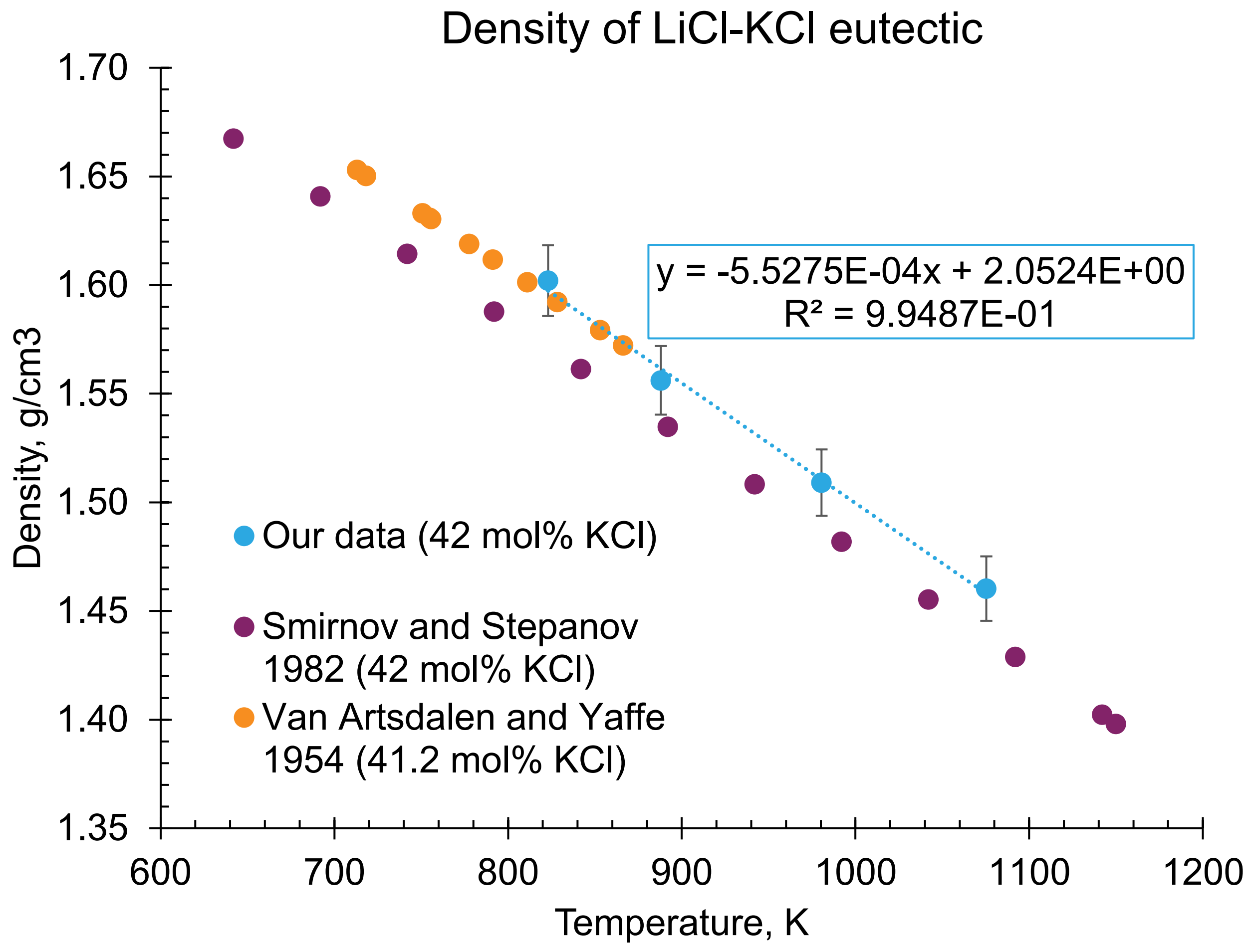
- Archimedes hydrostatic method

$$\rho_{salt} = \frac{M_{air} - W_{salt} + \frac{\pi D\gamma}{g}}{V_0[1 + \propto (T - T_0)]^3}$$

- M_{air} – mass as measured in Ar
- W_{salt} – weight in salt, average of five repeat measurements
- D – diameter of wire
- γ – surface tension of the salt
- g – acceleration due to gravity on Earth
- V_0 calculated in 10 mL of DI water and ethanol each by same method

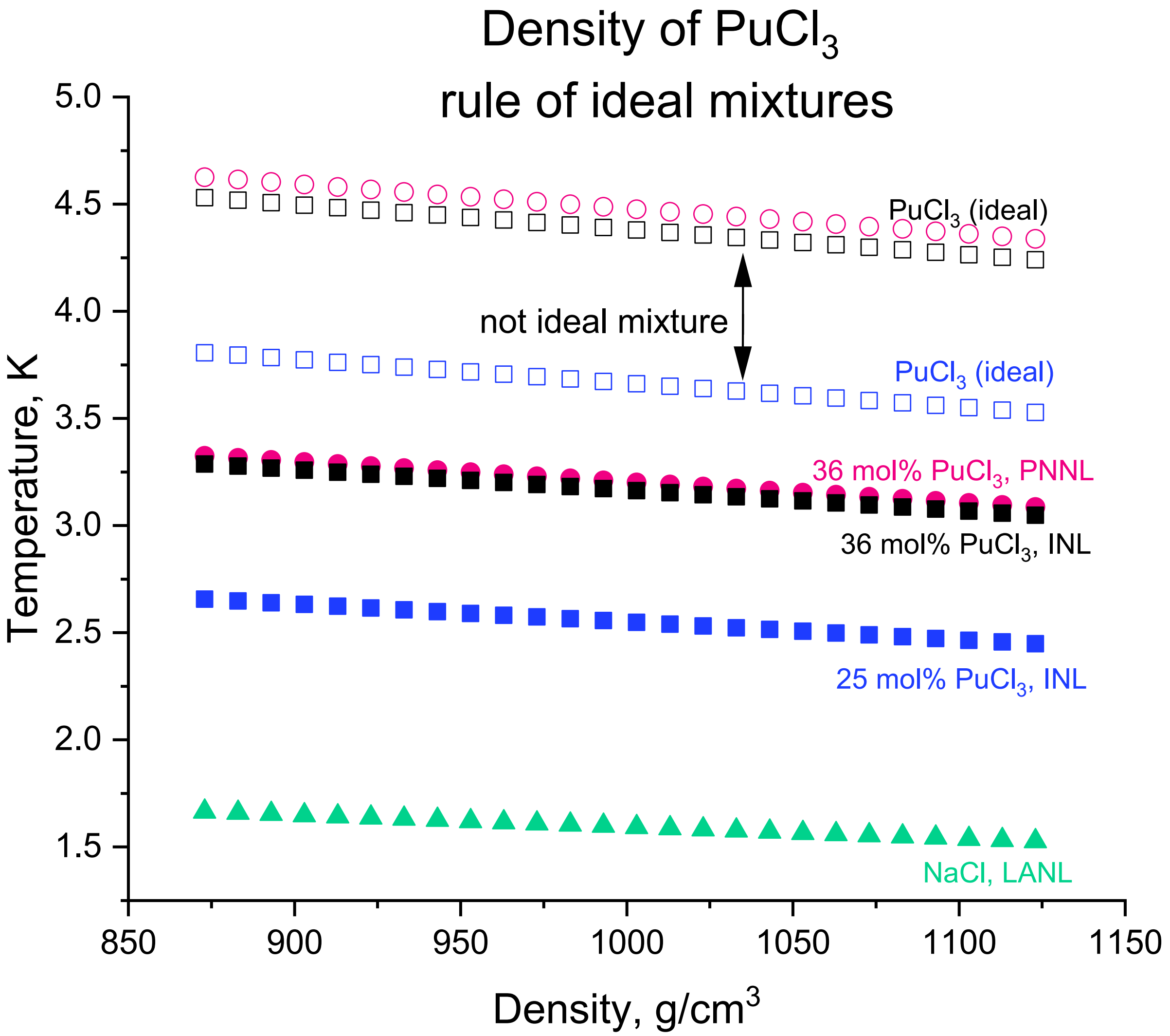
Density of $PuCl_3$-NaCl mixtures





Is it possible to assume the NaCl-$PuCl_3$ system behaves ideally? …No

- To estimate the density of a $PuCl_3$
  - Use rule of additive volume
  - Assume 36 mol% $PuCl_3$ and 25 mol% $PuCl_3$ are ideal mixtures
- Calculate density of $PuCl_3$ from mixtures of NaCl-$PuCl_3$
- Rule of additive volumes
  - $\frac{1}{\rho_{mix}} = \frac{w_{NaCl}}{\rho_{NaCl}} + \frac{w_{UCl_3}}{\rho_{UCl_3}}$
- Density of NaCl* and $PuCl_3$**
  - $\rho_{NaCl} = 2.147\frac{g}{cm^3} - 0.00055\frac{g}{cm^3 * K} * T(K)$
  - $\rho_{PuCl_3} = \frac{w_{PuCl_3}}{\frac{1}{\rho_{mix}} - \frac{w_{NaCl}}{\rho_{NaCl}}}$
- Mixtures of NaCl-$PuCl_3$ in this study - Not Ideal



Hydrostatic buoyancy method

- Many literature studies
  - Ignore the effect of surface tension

$$\frac{\pi D\gamma}{g}$$

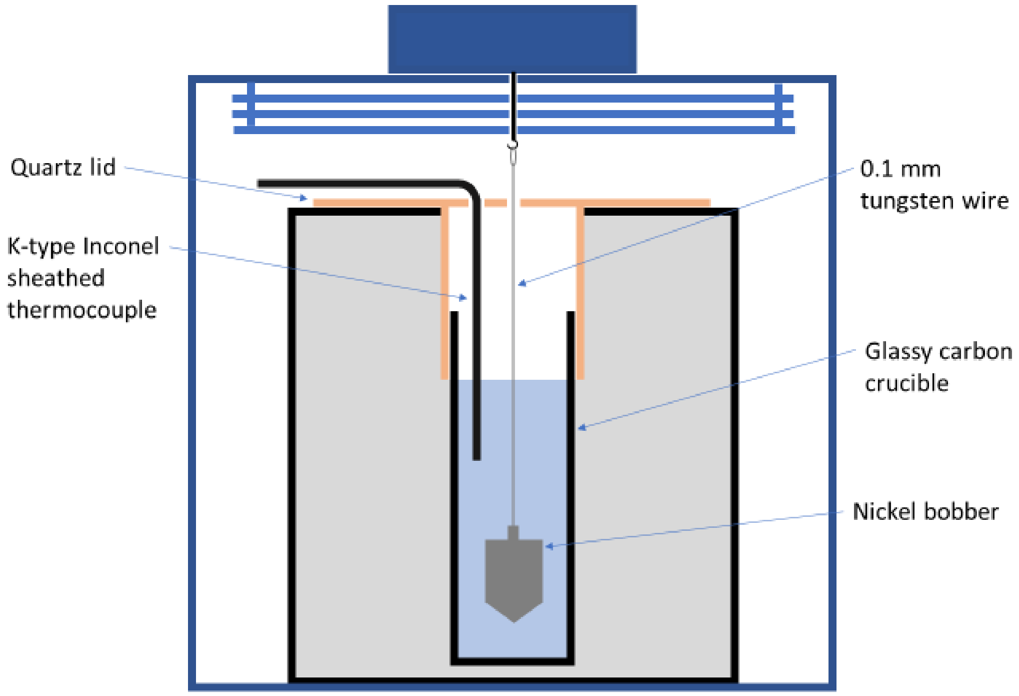
  - Approximate the volumetric expansion

$$\begin{aligned} V_0 + \Delta V &= (L_0 + \Delta L)^3 \\ &= L^3 + 3L^2\Delta L + 3L\Delta L^2 + \Delta L^3 \\ &\approx L^3 + 3L^2\Delta L \\ &\approx V + 3V\frac{\Delta L}{L} \\ &\approx V_0(1 + 3 \propto (T - T_0)) \end{aligned}$$

  - *How much of a contribution are these terms?*

- Archimedes hydrostatic method

$$\rho_{salt} = \frac{M_{air} - W_{salt} + \frac{\pi D\gamma}{g}}{V_0[1 + \propto (T - T_0)]^3}$$



Hydrostatic buoyancy method

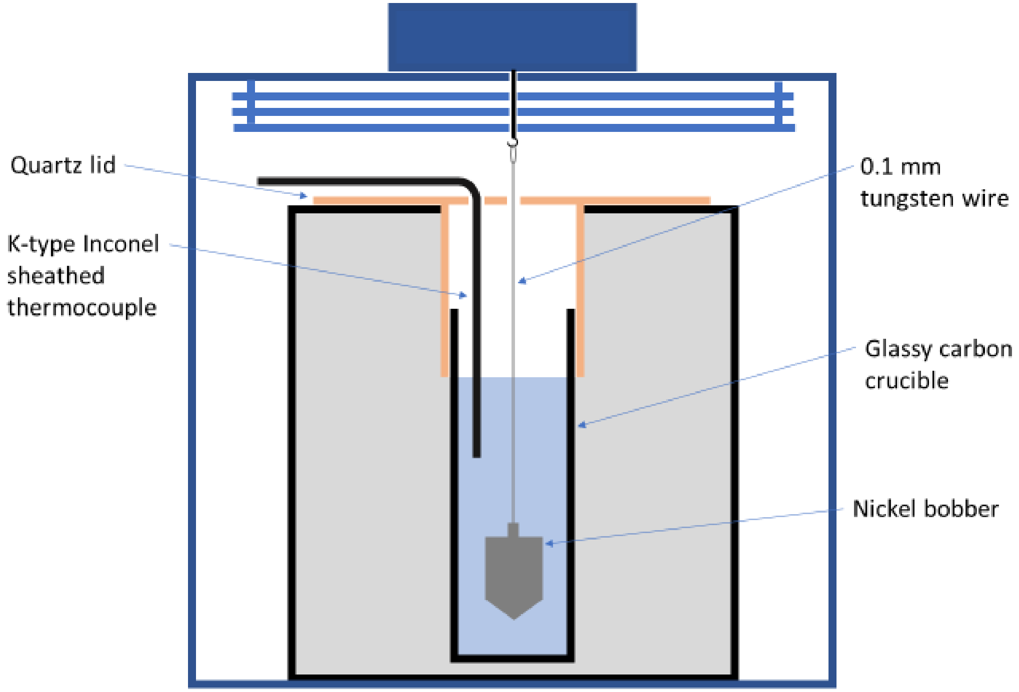
- Effect of surface tension $\frac{\pi D\gamma}{g}$

$$Assume$$
$$D = 0.01\ cm$$
$$\gamma \sim 0.120\,\frac{N}{m}$$
$$g = 980.7\ \mathrm{cm/s^2}$$
$$M_{air} - W_{salt} = 9.3165\ g - 6.3260\ g = 2.9905\ g$$
$$\frac{\pi D\gamma}{g} = 0.00384\ g$$

$$\%\,\boldsymbol{diff} = \left(\frac{\boldsymbol{\pi D\gamma}}{\boldsymbol{g}}\right)/(\boldsymbol{M_{air}} - \boldsymbol{W_{salt}}) = \mathbf{0.13}\ \%$$

- Archimedes hydrostatic method

$$\rho_{salt} = \frac{M_{air} - W_{salt} + \frac{\pi D\gamma}{g}}{V_0[1 + \propto (T - T_0)]^3}$$



Hydrostatic buoyancy method

- Volumetric expansion approximation

$$V_0 + \Delta V = (L_0 + \Delta L)^3$$
$$\approx V_0(1 + 3 \propto (T - T_0))$$

$$\boldsymbol{V_0(1 + 3 \propto (T - T_0))} \qquad \boldsymbol{V_0[1 + \propto (T - T_0)]^3}$$

$$Assume \quad V_0 = 1.039\ cm^3 \qquad \propto = 15.82 * 10^{-6} \frac{m}{m*°C}$$
$$T - T_0 = 680°C$$

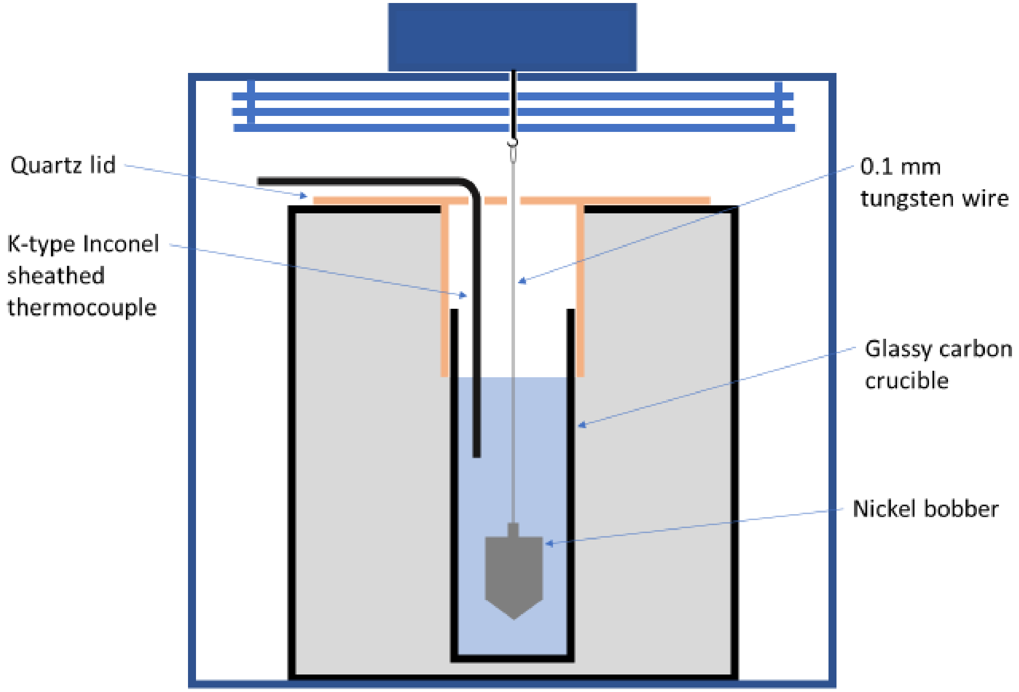
$$\boldsymbol{V_0(1 + 3 \propto (T - T_0)) = 1.073\ cm^3}$$

$$\boldsymbol{V_0[1 + \propto (T - T_0)]^3 = 1.073\ cm^3}$$

$$\% \boldsymbol{\ diff\ is\ negligible}$$

- Archimedes hydrostatic method

$$\rho_{salt} = \frac{M_{air} - W_{salt} + \frac{\pi D \gamma}{g}}{V_0[1 + \propto (T - T_0)]^3}$$



Corrosion of the bobber

- How much does the volume of the bobber change due to corrosion over the course of measurements?

$$Surface\ Area = 5.7cm^3$$

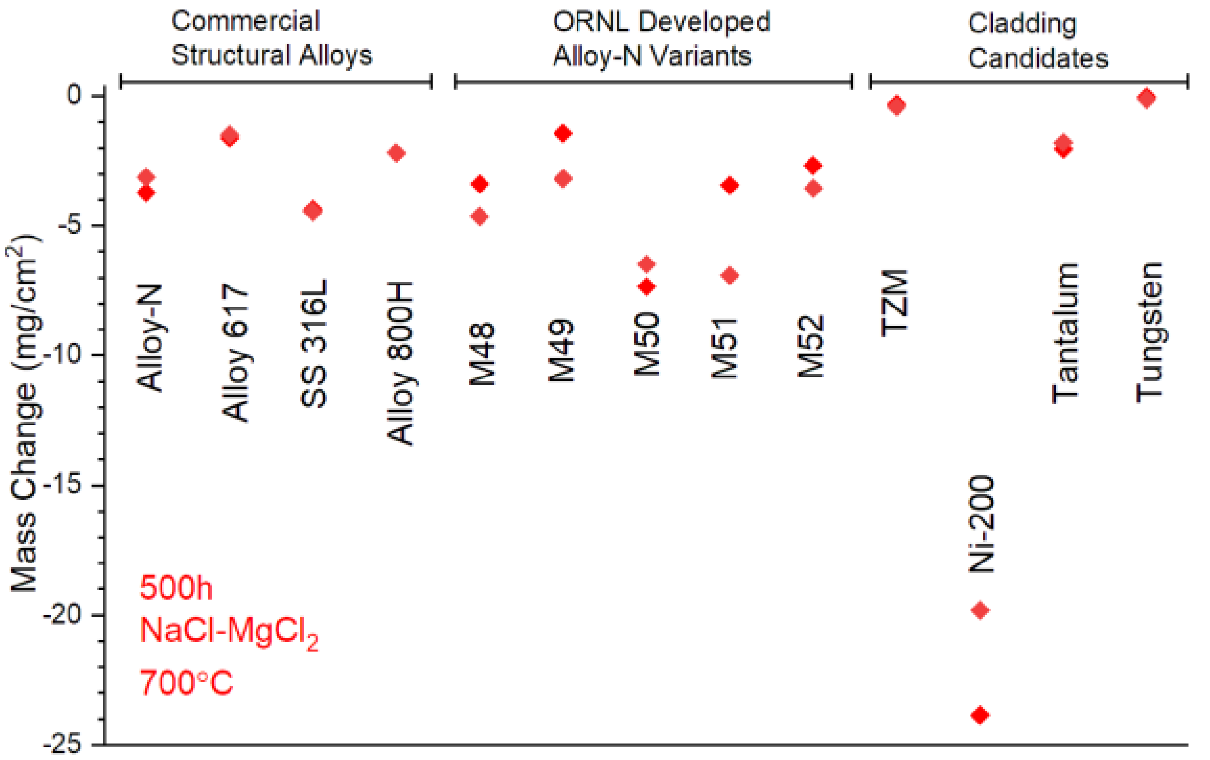
$$Corr.rate = 0.044\ \frac{mg}{cm^3 * hr}$$

$$Assume\ 30\ hr\ equivalent\ exposure$$

$$Mass\ loss = 7.5\ mg$$

$$Assume\ M_0 = 9.3\ g$$

$$\%\ diff = 0.081\%$$



"Compatibility Studies of Cladding Candidates and Advanced Low-Cr Superalloys in Molten NaCl-MgCl2", ORNL/TM-2019/1132, (2019)

Funding Acknowledgments & Contact

- This work was supported by the Molten Salt Reactor Campaign, work package number AT-22IN070502 “Thermochemical and Thermophysical Property Database Development – INL”

- This work was supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

- Michael.Woods@inl.gov

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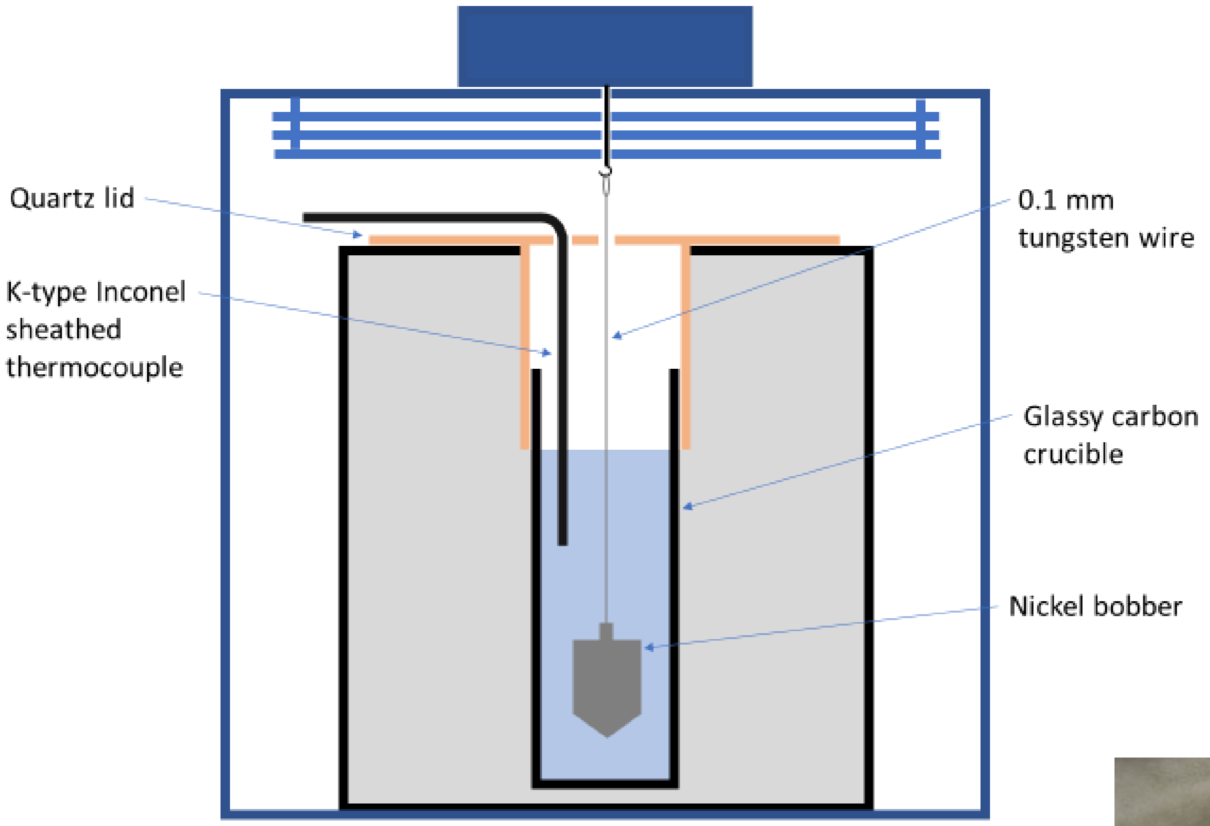
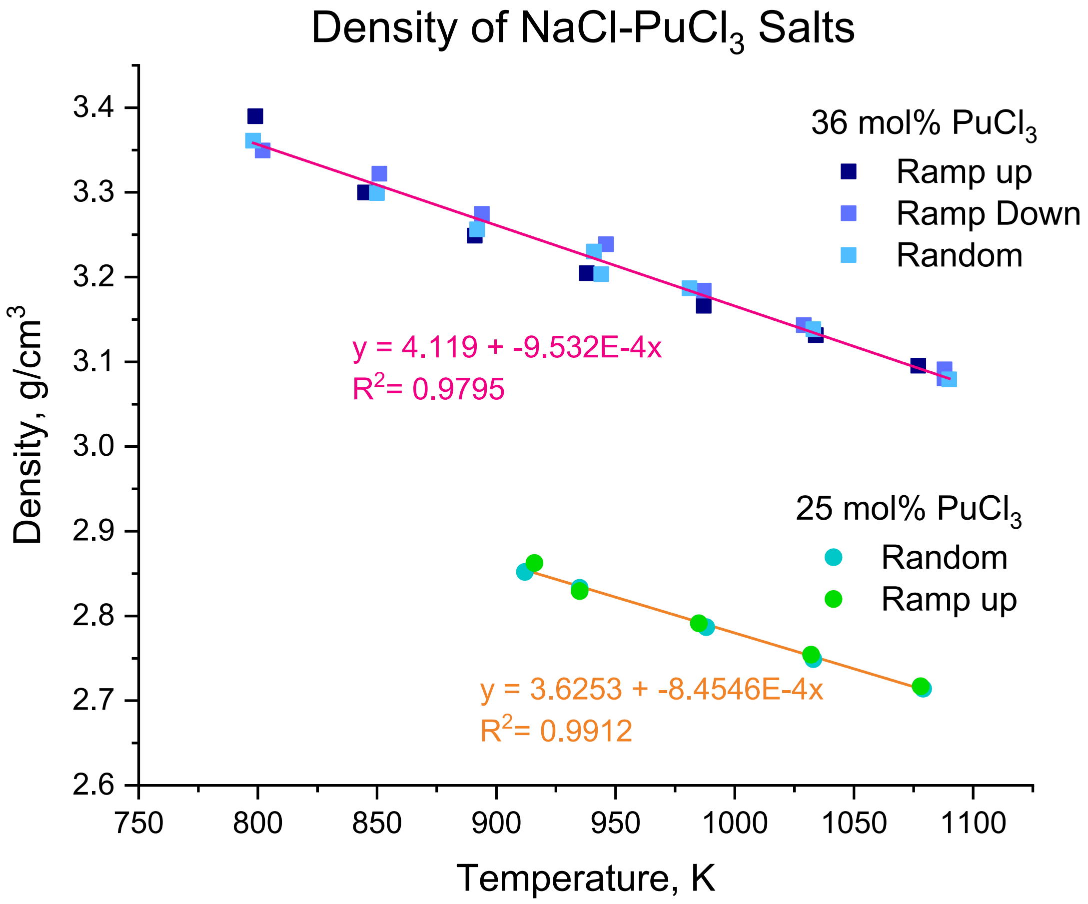
Density of $PuCl_3$-NaCl mixtures



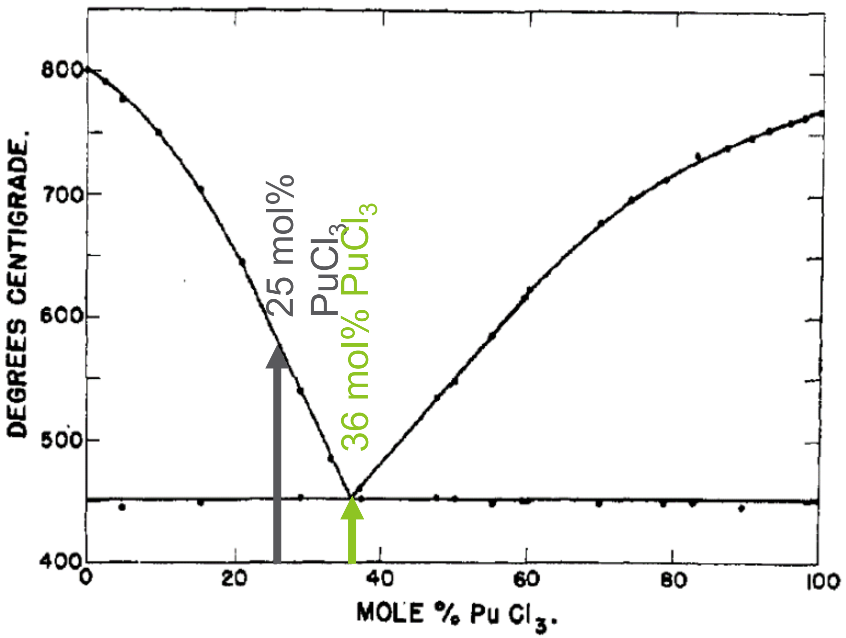


- Archimedes' hydrostatic method

$$\rho_{salt} = \frac{M_{air} - W_{salt} + \frac{\pi D \gamma}{g}}{V_0[1 + \propto (T - T_0)]^3}$$

Elemental/Isotopic Analysis

- Elemental analysis of starting material metal and salt
  - ICP-OES with TEVA separation
  - ICP-MS
  - Gamma Spec for Am^{241}
- Composition
  - 63.3 mol% NaCl (22.6 wt%)
  - 36.2 mol% $PuCl_3$ (76.4 wt%)
  - 0.5 mol% other (1.05 wt%)
    - ($FeCl_3$, UCl_3, $NpCl_3$, $AmCl_3$)
- Purity of salt is 99.5%
- Eutectic composition predicted from Bjorklund et al.
  - 64 mol% NaCl – 36 mol% $PuCl_3$



Bjorklund, C. W., Reavis, J. G., Leary, J. A., Walsh, K. A. "Phase Equilibria in the Binary Systems $PuCl_3$-NaCl and $PuCl_3$-LiCl" 1959

	Pu-metal		$NaCl-PuCl_3$ Eut. Salt	
Analyte	ug/g	% Error	ug/g	% Error
U-234	118	±10%	60.4	±10%
U-235	792	±5%	406	±5%
U-236	556	±5%	283	±5%
m/z-238	430	±5%	246	±5%
Np-237	390	±5%	212	±5%
Pu-239	807000	±5%	469000	±5%
Pu-240	157000	±5%	91600	±5%
m/z-241	10100	±5%	6040	±5%
m/z-242	3350	±5%	1960	±5%
Sr-88	<40	N/A	8.06	±15%
m/z-107	14.3	±30%	12.7	±15%
Ag-109	10.7	±20%	11.7	±20%
Fe	91.0	± 25 %	72.7	± 30 %
Na	<320	N/A	94900	±5%
Pr	<30	N/A	83.8	± 20 %
	Pu-metal		$NaCl-PuCl_3$ Salt	
Analyte	uCi/g	% Error	uCi/g	% Error
Am-241	2.51E+0 4	±3%	1.41E+0 4	±3%
Np-239	<7E-1	±3%	<3E-1	N/A