Molten Salt Reactor Campaign FY25 Report

Drop Calorimetry of Actinide-Bearing Chloride Salts

Bryn E. Merrill
Andrew C. Strzelecki
Hannah K. Patenaude
S. Scott Parker
Marisa J. Monreal

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Prepared by: Bryn E. Merrill, Graduate Research Assistant
Analytical Earth Sciences (EES-15)

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1 Introduction

The following report outlines work completed by the Los Alamos National Laboratory (LANL) towards the mission set forth by the U.S. Department of Energy – Nuclear Energy (DOE-NE) Molten Salt Reactor (MSR) Campaign, which is to develop the technological foundations needed to enable safe and economical operations of MSRs while maintaining a high level of proliferation resistance. The DOE-NE MSR Campaign serves as the hub for efficiently and effectively addressing, in partnership with other stakeholders, the technology challenges for MSRs to enter the commercial market. The MSR Campaign supports experimental and computational efforts to characterize molten salt systems relevant to reactor operation, safety, and maintenance, including, but not limited to, thermophysical properties measurements of actinide (An)-bearing salts. The inherent challenges of measurements in high temperature, corrosive molten salt environments require meticulous preparation for carefully planned experiments to provide reliable data that can support MSR design, computational models, and licensing.

Understanding fundamental thermodynamic properties such as the heat capacity (C_p), enthalpy of mixing (ΔH_{mix}), enthalpy of fusion (ΔH_{fus}), and phase transitions of An-bearing molten salts are of utmost importance to the MSR community. Experimental data are necessary to validate and improve advanced models such as molecular dynamics (MD) simulations and CALculated PHAse Diagrams (CALPHAD) methods powered by resources like the Molten Salt Thermal Properties Database (MSTDB).[1–3] This report includes experimental progress at Los Alamos National Laboratory (LANL), where high temperature transpose drop (TTD) calorimetry was the primary technique for characterizing plutonium and uranium-bearing chloride salt systems for the MSR Campaign. The TTD calorimetry excess heat capacity measurements recently published for this project on the $PuCl_3$-NaCl binary eutectic in collaboration with Idaho National Laboratory (INL) is first summarized, followed by an overview of ongoing efforts to determine heat capacity and enthalpy of mixing (ΔH_{mix}) of the UCl_3-NaCl pseudobinary system. These studies are foundational to the continued exploration of An chloride salt properties that are needed to ultimately expand the available information needed by the MSR community.

2 High Temperature Transpose Drop (TTD) Calorimetry

High temperature transpose drop (TTD) calorimetry measurements can provide essential experimental data and thermodynamic information for MSR fuels, such as $PuCl_3$-NaCl and UCl_3-NaCl. This information can aid modelling efforts and provide baseline data for more complex fuel salt mixtures, such as ternary or higher order mixtures.

2.1 $PuCl_3$-NaCl Eutectic Calorimetry

Despite many years of research on the thermodynamic properties of molten salts, there are still limited thermodynamic data of molten salt mixtures containing $PuCl_3$. This lack of data is likely due to several factors, including inherent challenges like the scarcity of Pu materials, scientific expertise, and experimental capabilities.

2.1.1 *Materials and Methods*

The $PuCl_3$-NaCl eutectic mixture was synthesized at INL. The procedure has been reported in detail elsewhere,[4] and is briefly summarized as follows. The NaCl (99.99%) was heated under vacuum at 623 K for 3.5 h in a high-purity argon atmosphere and NH_4Cl (99.99%) was heated at 473 K for 8 h. The Pu metal

was purified via a hydriding-dehydriding reaction to remove any potential oxide impurities. The $PuCl_3$-NaCl eutectic mixture was prepared by mixing NaCl, NH_4Cl, and Pu in a glassy carbon crucible. The amount of NH_4Cl used in the chlorination was in excess of 2 wt% with respect to NaCl to ensure complete chlorination of Pu. The mixture was then heated to 1073 K over a period of 60 h at a ramp rate of 5 $K \cdot min^{-1}$, then allowed to cool to room temperature. This yielded an ingot of composition equal to 36 mol% $PuCl_3$ and 64 mol% NaCl.

The $PuCl_3$-NaCl eutectic mixture was shipped from INL to Los Alamos National Laboratory (LANL) in a welded stainless-steel tube and subsequently stored and processed in inert, negative-pressure, dry gloveboxes.[5] Phase purity was initially assessed at INL using ICP-OES, ICP-MS, Gamma spectroscopy, XRD, and DSC,[4] and confirmed at LANL with DSC.[5] Drop-calorimetric measurements of the $PuCl_3$-NaCl eutectic mixture were performed using the method developed for chloride salts by Strzelecki et al.[6] The samples were loaded into Ni capsules and then double-fold sealed in an inert negative pressure dry glovebox. Smooth-wall flat-bottom Ni 270 alloy (99.95% Ni) capsules (14.5 × 7 mm, Elemental Microanalysis, Devon, United Kingdom) were used as the encapsulating containers. The Ni capsules loaded with the $PuCl_3$-NaCl eutectic mixtures were transferred from the inert negative pressure dry glovebox to an open-facing fume hood and then placed into polyvinylchloride (PVC) ball valves (Figure 2-1) and sealed. The masses of Ni capsules and $PuCl_3$-NaCl in each capsule are reported in Table 1. The PVC ball valves acted both as a secondary encapsulation layer and as a sample seal-and-drop device, similar to that used in previous drop-calorimetric measurements of PuO_2.[7]

Figure 2-1. Two polyvinylchloride (PVC) ball valve droppers mounted onto the glassware of the Setaram AlexSYS-800 drop calorimeter.

Table 1. High-temperature transposed-temperature drop-calorimetric results of the $PuCl_3$-NaCl eutectic mixture at 976 K. As the Setaram AlexSYS-800 calorimeter is of twin-Calvet type, it has two calorimetric chambers denoted by the left and right sides. The calibration constant of the left chamber was –0.0049942 $J \cdot \mu V^{-1} \cdot s^{-1}$ and that of the right chamber was 0.0049959 $J \cdot \mu V^{-1} \cdot s^{-1}$.

Two replicates were dropped on each side of the calorimeter. The heat of the Ni capsules used in the correction was taken from Strzelecki et al.[6]

	Left Side		Right Side	
	Replicate #1	Replicate #3	Replicate #2	Replicate #4
Nickel capsule mass (mg)	512.98	514.69	512.11	512.4
Nickel ($\times 10^{-3}$ mols)	8.7400	8.7691	8.7252	8.7301
NaCl+$PuCl_3$ eutectic mass (mg)	17.16	15.21	16.61	17.19
NaCl+$PuCl_3$ eutectic ($\times 10^{-4}$ mol)	1.056	0.9363	1.023	1.058
T_{Room} (K)	296.16	296.42	296.41	295.38
T_{Cal} (K)	975.69	975.8	975.73	975.86
Integrated signal (μV·s)	−42521	−42523	42,740	42,664
Uncorrected ΔH (J)	212.36	212.37	213.53	213.15
ΔH of Ni (J)	197.02	197.68	196.69	196.8
Corrected ΔH (J)	15.34	14.69	16.84	16.35
ΔH_{ttd} (kJ·mol^{-1})	145.19	156.9	164.68	154.48
Average ΔH_{ttd} (kJ·mol^{-1})	155.31			
2σ ΔH_{ttd} (kJ·mol^{-1})	8.03			

The transpose temperature drop enthalpies (ΔH_{ttd}) were directly measured using a Setaram AlexSYS-800 Tian-Calvet twin microcalorimeter with two sample chambers (Caluire-et-Cuire, France).[8–12] ΔH_{ttd} is the sum of the enthalpic increments and the enthalpy associated with any thermal event, such as the enthalpy of fusion (ΔH_{fus}).[13] The ΔH_{ttd} values were measured for all the samples listed in Table 1 at 975.77 ±0.08 K. A calibration factor (J·μV^{-1}·s^{-1}) was needed to convert the measured heat to ΔH_{ttd} (kJ·mol^{-1}) at this temperature. The calibration factors for both sample chambers were determined by measuring the ΔH_{ttd} values of α-Al_2O_3 and Au and comparing the results with literature values.[14] During the drop-calorimetric measurements, the calorimeter glassware was allowed to purge for at least 10 mins with high purity Ar flushing at ~2 L·min^{-1}, after which the flushing rate was lowered to ~200 mL·min^{-1} and fixed at this rate for the duration of the experiment.

There is an accepted empirical approximation method for determining C_p values of molten salt systems. In this method, the C_p of a multicomponent salt mixture can be approximated by a sum of the C_p values of single constituents (e.g., NaCl and UCl_3).[15,16] This approximation is referred to as the mole-fraction average method,[15,16] or the Neumann-Kopp's rule (NKR),[17] and is illustrated in equation 1:

$$C_p = \Sigma x_i C_{p,i} \quad \text{Eq. 1}$$

where x_i and C_p are the molar fraction and heat capacity, respectively, of the ith component. Using this method, the heat capacity of the molten $PuCl_3$-NaCl eutectic mixture was approximated to be 97.7 J·mol^{-1}·K^{-1}, where the C_p for $PuCl_3$ was taken from Beneš and Konings,[18] and that for NaCl from Chase.[14] This method can be extended to describe the theoretical interaction between molten NaCl and $PuCl_3$ under ideal conditions, with no excess thermodynamic quantities resulting from their interaction.

2.1.2 *Results*

The ΔH_{ttd} of the $PuCl_3$-NaCl eutectic mixture (36.3 mol% $PuCl_3$ and 63.7 mol% NaCl) was measured at a calorimeter temperature of 975.77 ±0.08 K. Measurements were performed as four replicates and an average value is reported below. The ΔH_{ttd} of $PuCl_3$-NaCl eutectic from 296.47 ±0.21 to 975.77 ±0.08 K was determined to be 155.31 ±8.03 kJ·mol^{-1}, after subtracting the enthalpic effect of the Ni capsule, by four drop-calorimetric measurements (Table 1). Within this single corrected ΔH_{ttd} value is the $\Delta H_{726\text{-}298.15}$ of the solid eutectic mixture, the ΔH_{fus} of the eutectic mixture, and the $\Delta H_{T\text{-}726}$ of the liquid eutectic mixture.

The integral heat capacity of the solid eutectic mixture was calculated using the NKR,[19] using literature values for the heat capacities of solid $PuCl_3$[18] and NaCl.[14] The upper temperature limits of the C_p integration for $PuCl_3$ and NaCl are the average onset melting temperature (726 ±3 K) for the eutectic $PuCl_3$-NaCl mixture.[4,5,18,20,21] The derived $\Delta H_{T\text{-}298.15}$ values of solid $PuCl_3$ and NaCl are 47.4 kJ·mol^{-1} and 23.2 kJ·mol^{-1}, respectively. Applying NKR, the integral heat capacity of the solid $PuCl_3$-NaCl eutectic is determined to be 32.0 kJ·mol^{-1}.[14,18]

Subtracting the recommended ΔH_{fus} (21.8 ±1.6 kJ·mol^{-1}, Table 1), and the integral heat capacity of the solid eutectic mixture (32.0 kJ·mol^{-1}), approximated using NKR, from the experimentally determined ΔH_{ttd} (155.31 ±8.03 kJ·mol^{-1}) yields a $\Delta H_{T\text{-}726}$ of the molten $PuCl_3$-NaCl eutectic mixture to be 101.5 ±8.1 kJ·mol^{-1} at 976 K (Figure 2-2a). To better define the $\Delta H_{T\text{-}726}$ trend (Figure 2-2a), it would be ideal to have more $\Delta H_{T\text{-}726}$ values between 923 and 976 K, and even at >976 K. However, the resource-intensive nature of transpose temperature drop-calorimetric experiments on Pu-bearing samples precluded additional measurements of molten $PuCl_3$-NaCl eutectic at this time. We intend to conduct such measurements at selected additional temperature points (especially >976 K) in the future. In the meantime, another means of determining the heat capacity is through calculating the mean heat capacity (C_m)[22] using equation 2.

$$C_m = \frac{H_{T,cal} - H_{298}}{T_{cal} - 298} \qquad \text{Eq. 2}$$

In doing so, the C_m at 975.77 ±0.08 K is determined to be 104.0 ±8.3 J·mol^{-1}·K^{-1} (Figure 2-2b).

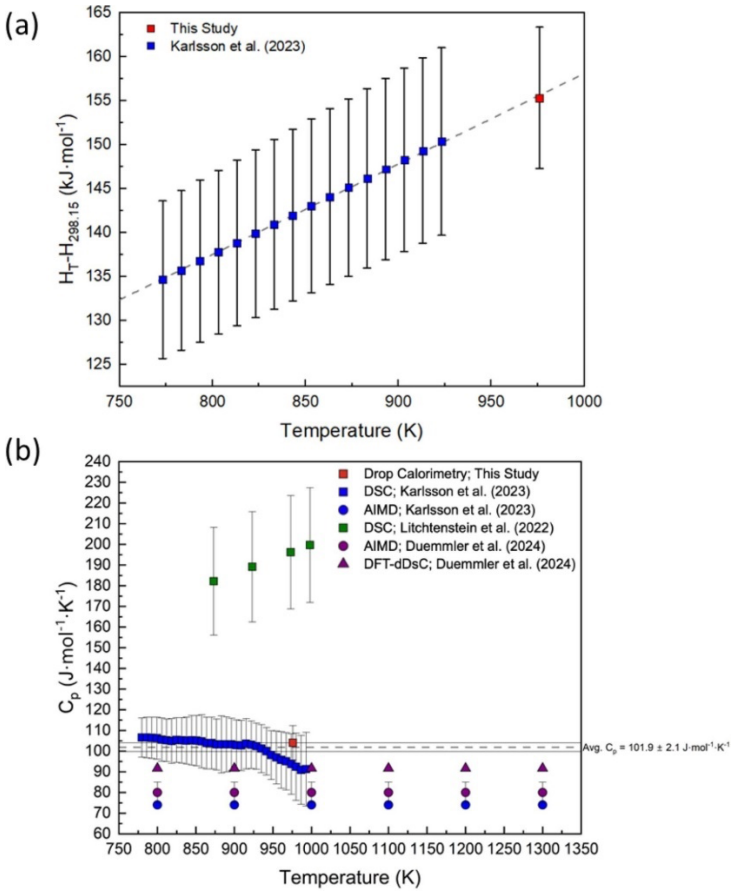

Figure 2-2. Measured thermodynamic values of $PuCl_3$-NaCl eutectic from this study compared to literature values. (a) The enthalpy increment of the $PuCl_3$-NaCl eutectic mixture measured at 976 K in this study, together with previous measurements at lower temperatures by Karlsson et al.,[4] which used DSC. (b) The heat capacity (C_p) data of the $PuCl_3$-NaCl eutectic mixture in Karlsson et al.[4] and Duemmler et al.[23,24], and the C_p data of 0.374$PuCl_3$-0.626NaCl in Lichtenstein et al.,[21] compared to the average heat capacity determined in this study.

The determined C_p (101.9 ±2.1 J·mol^{-1}·K^{-1}) of the molten $PuCl_3$-NaCl eutectic mixture is larger than that approximated by the mole-fraction average method (97.7 J·mol^{-1}·K^{-1}). However, as explained by Capelli et al.,[25] Beneš et al.,[26] and Beilmann et al.,[27] for alkali-alkali and alkali-alkaline earth fluoride mixtures (e.g., LiF-NaF and LiF-CaF_2), a deviation between experimental C_p and that derived by the mole-fraction average method is a result of the contribution of excess heat capacity (C_p^{ex}) of the liquid solution. This deviation also occurs for the molten $PuCl_3$-NaCl eutectic mixture, and its (C_p^{ex}) is derived to be 4.2 ±2.1 J·mol^{-1}·K^{-1}.

Yin et al.[28] stated that the enthalpy of mixing (ΔH_{mix}) of a binary chloride system may be predicted using equation 3:

$$\Delta H_{mix} = f(\delta_{12});$$
$$\delta_{12} = [r_{Ak^+} - \gamma_{An^{3+}}]/[(r_{Ak^+} + r_{Cl^-})(r_{An^{3+}} + r_{Cl^-})] \quad \text{Eq. 3}$$

where δ_{12} refers to the function of the ionic parameters, and r_{Ak^+} and $r_{An^{3+}}$ are the ionic radii of alkali (e.g., Na^+) and actinide cations (e.g., Pu^{3+}), respectively, in a six-fold coordination. Using this equation and the ionic radii in Shannon,[29] a δ_{12} of 0.02515 nm^{-1} for $PuCl_3$-NaCl was obtained. Yin et al. derived the function,

$f = -3477.2 \cdot \delta_{12} - 5220.6$ J·mol^{-1}, which relates δ_{12} to $f(\delta_{12})$ and thus ΔH_{mix} of NaCl-MCl_3 (where M is a metal cation with a trivalent charge).[30] Using this equation, ΔH_{mix} for $PuCl_3$-NaCl would be −5.3 kJ·mol^{-1}. Redkin et al. stated that a linear relation exists between C_p^{ex} and ΔH_{mix},[31] while Yingling et al. employed an exponential relation as the value of ΔH_{mix} approaches 0.[32] Previously, Karlsson et al. found that when using the ΔH_{mix} reported in Schorne-Pinto et al. (ΔH_{mix} = -7.3 kJ·mol^{-1}) , their value of C_p^{ex} falls within the error along the exponential trend of Yingling et al. (Figure 2-3), .[4,32,33] As the C_p equation reported by Karlsson et al. has been updated in this study, so has the C_p^{ex}. Note the C_p^{ex} (4.2 ±2.1 J·mol^{-1}·K^{-1}) determined in this study is in good agreement with the predicted value of Yingling et al.,[32] when using the ΔH_{mix} determined by the method of Yin et al. (ΔH_{mix} = -5.3 kJ·mol^{-1}).[30]

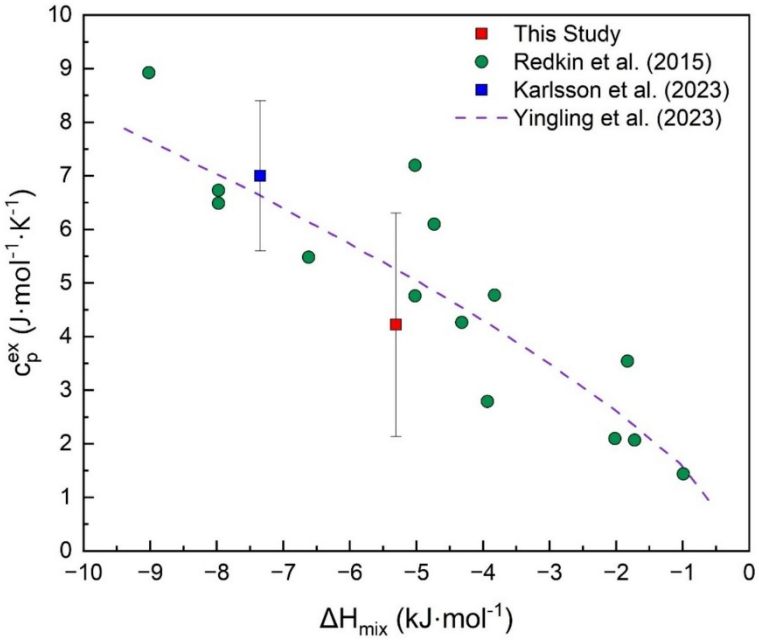

Figure 2-3. Relationship between C_p^{ex} and ΔH_{mix}. The red square denotes the C_p^{ex} determined here and the ΔH_{mix} determined by Yin et al.,[30] the green circles denote the values estimated by Redkin et al.,[31] the blue square is the C_p^{ex} determined by Karlsson et al.,[4] and the ΔH_{mix} determined by Schorne-Pinto et al.,[33] and the purple dashed line represents the exponential equation given by Yingling et al.[34]

2.1.3 *Concluding Remarks*

The transposed temperature drop enthalpy (ΔH_{ttd}) of the $PuCl_3$-NaCl eutectic mixture was directly measured using a commercial Tian-Calvet twin microcalorimeter with two sample chambers (Setaram AlexSYS-800) and the Ni encapsulation technique. The ΔH_{ttd} was found to be 155.31 ±8.03 kJ·mol^{-1} at 975.77 ±0.08 K. To verify this ΔH_{ttd} value, a critical assessment of the related thermochemical parameters from the literature was made.[4,5,20,21,23,24,33] Using these data, the $\Delta H_{T\text{-}726}$ of the molten $PuCl_3$-NaCl eutectic mixture was determined to be 101.5 ±8.1 kJ·mol^{-1}, which agrees well with the C_p derived by Karlsson et al. using differential scanning calorimetry.[4] The original C_p equation of Karlsson et al. was then extended with confidence to 998 K, yielding C_p = 101.9 ±2.1 J·mol^{-1}·K^{-1} at this temperature.[4] These findings confirm the results of Karlsson et al.[4]and Duemmler et al.,[23,24] which indicate that the C_p of the molten $PuCl_3$-NaCl eutectic mixture exhibits no temperature dependence. Moreover, the C_p^{ex} of molten $PuCl_3$-NaCl was determined to be 4.2 ±2.1 J·mol^{-1}·K^{-1}, which was then used to derive its ΔH_{mix} to be –5.3 kJ·mol^{-1}. These results provide the basis for modeling the thermodynamic stability of molten species in the $PuCl_3$-NaCl system for nuclear energy and other applications.

2.2 Experimental Adaptations

The methodology used in the $PuCl_3$-NaCl eutectic calorimetric measurements were found to be both safe and effective. During these measurements, it was recognized that the large mass difference between the nickel capsules and the salt samples (Table 1) presented an opportunity to further improve accuracy while also reducing measurement uncertainty. Smaller, 7 × 3.5 mm nickel capsules from Alpha Resources have thus been implemented for the UCl_3-NaCl experiments. While still possessing greater mass than the salt samples (~132 mg vs. ~20 mg), the 7 × 3.5 mm capsules produce a smaller heat response, reducing the difference in heat response between the nickel capsules and the salt samples. These capsules are folded in the glovebox in the same manner as the larger 14.5 × 7 mm capsules used for the $PuCl_3$-NaCl, therefore continuing to serve the dual purpose of protecting the sample from the atmosphere and preventing contamination by containing the sample.

The setup for the $PuCl_3$-NaCl experiment displayed in Figure 2-1 shows the nickel-encapsulated samples enclosed inside the PVC ball valves which act as secondary containment for the samples. Other air-free droppers and methods for air-free calorimetry have been designed in the past, including the sample seal-and-drop device from Guo et al. that was used for PuO_2 measurements.[7] For the $PuCl_3$-NaCl eutectic work, the connection between the PVC ball valve and the fused quartz setup was developed using computer-aided design (CAD) software in several 3D-printed parts that were then assembled with glue. These connections were packed with the $PuCl_3$-NaCl waste, and could not be reused. To more efficiently produce these connections for future radioactive salt work, a new design was created in CAD that produced the entire connection in one part (Figure 2-4). This design was based upon the connection used for the $PuCl_3$-NaCl experiments, however, a few key changes were made with regards to the number of o-rings and their placement, as well as the HEPA filter connection. The original connection had space for four o-rings on the insert for the glassware and no o-ring for the connection to the PVC attachment for the ball valve. Figure 2-4 shows the glassware insert on the new design has slots for two o-rings, which will still provide the necessary seal and stability for the connection. The top of the connection on the new design also has space for an o-ring which will provide stability for the PVC ball valve dropper and will add extra security for more volatile species of interest for future studies, such as UCl_4, during measurements at temperatures above melting.

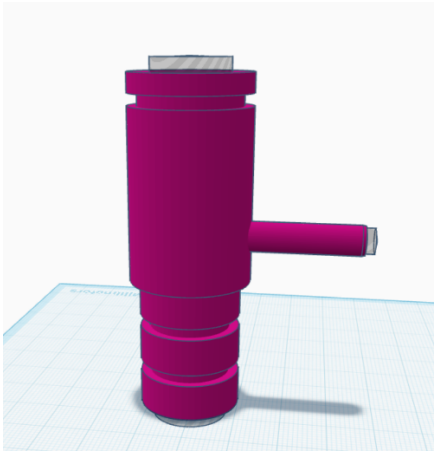

Figure 2-4. 3D CAD drawing of the updated PVC connector for future molten salt experiments.

While the HEPA filter is not necessary for measurements involving depleted uranium compounds, the adapted design incorporates the HEPA filter connection in preparation for further plutonium salt work and volatile compounds. Two of these custom connectors have been printed in-house, in the LANL Rapid

Prototyping Laboratory, demonstrating that the whole connector can be printed at once, increasing efficiency for single use experiments as printed parts do not need to be glued together and dried before use.

2.3 UCl_3-NaCl Eutectic Calorimetry

Current experimental literature data available for the phase boundaries of the UCl_3-NaCl system has primarily been collected using DSC and phase transition analysis methods.[3,32,35–37] Discrepancies on the phase boundaries in the literature stem from the variance in the experimental data, inciting debate on the existence of an intermediate compound in this binary system. Experimental mixing data on this system is minimal, and modelling efforts such as MD simulations and CALPHAD methods are limited to one experimental mixing dataset.[2,38,39]

2.3.1 *Methods*

UCl_3 purity was confirmed as reported previously[40] and high-purity (>99.99%) NaCl was purchased from Sigma-Aldrich. The NaCl was dried in an antechamber vacuum oven connected to the glovebox at 393 K for 24 hours followed by another 24 hours at 493 K.[41]

The integral heat capacity or enthalpic increment ($\Delta H_{T\text{-}1064}$) from room temperature (296.50 $\pm$0.08 K) to the calorimeter temperature (1064.61 $\pm$0.04 K) was measured for both endmember salts and pure nickel in the high temperature drop calorimeter using the encapsulation method described in Section 2.1.1 and smooth-walled 7 mm by 3.5 mm pure nickel capsules from Alpha Resources. The nickel capsules were cleaned by submerging them in reagent grade alcohol and sonicating the solution for five minutes. They were then dried in a 423 K oven for 10 minutes before being moved into a positive pressure, inert argon glovebox (<1 ppm O_2 and H_2O).

The endmember samples were prepared by loading clean nickel capsules with 20-30 mg of one of the endmember salts while the eutectic samples were prepared by loading approximately 15 mg of UCl_3 into each capsule and then the corresponding NaCl to create 34-66 mol% UCl_3-NaCl eutectic mixtures. The nickel capsules, both with sample and empty, were sealed by pinching the top of the capsule shut and then folding the pinched part over twice using pliers. The eutectic samples, once sealed in the nickel capsules, were shaken to mix before being closed in PVC ball valves for transport and dropped into the calorimeter akin to the other sealed samples.

The Setaram AlexSYS-800 Tian-Calvet twin microcalorimeter, similar to what is shown in Figure 2-5, was calibrated using empty nickel capsules and existing literature data from NIST.[14] Ultra-high purity argon gas was flushed through the calorimeter setup to prevent the oxidation of the nickel capsules during experimentation for both the empty nickel capsule experiments and salt experiments.

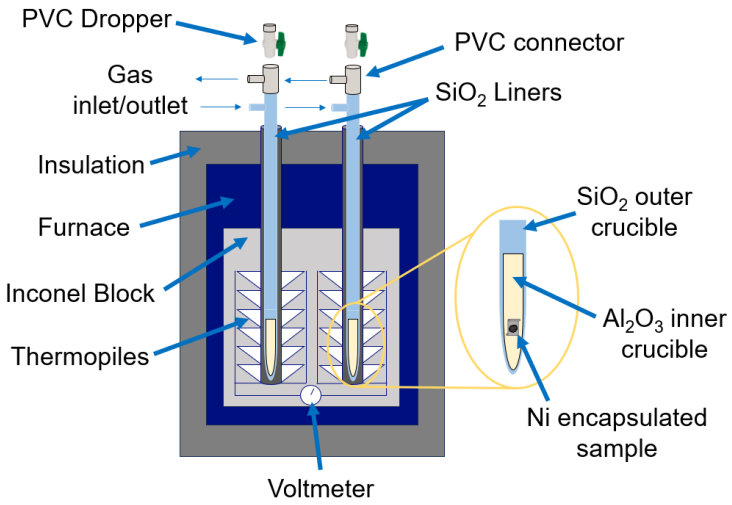

Figure 2-5. Schematic of Seteram AlexSYS high temperature drop calorimeter and experimental setup for TTD calorimetric measurements.

2.3.2 *Results*

Pure nickel and pure NaCl are well studied, and thermodynamic literature data is widely available for both compounds. Heat capacity data collected by Chase in 1998 from these two compounds have been fit with the Shomate equation shown here as equation 4, where t is the temperature in K divided by 1000.[41]

$$C_p = A + B * t + C * t^2 + D * t^3 + \frac{E}{t^2} \qquad \text{Eq. 4}$$

The coefficients for the Shomate equation are tabulated in the NIST Chemistry Webbook and have been reproduced here for nickel and sodium chloride in Table 2.[42]

Table 2. NIST Chemistry Webbook Shomate equation coefficients for solid nickel and sodium chloride using data collected in 1998 from Chase.[42]

	Solid Ni (298-600 K)	Solid Ni (600-700 K)	Solid Ni (700-1728 K)	Solid NaCl (298-1073 K)
A	13.69160	1248.045	16.49839	50.72389
B	82.49509	−1257.510	18.74913	6.672267
C	−174.9548	0.000000	−6.639841	−2.517167
D	161.6011	0.000000	1.717278	10.15934
E	−0.092417	−165.1266	1.872051	−0.200675

The pure UCl_3 integral heat capacity was theoretically calculated using the heat capacity fitting coefficients from the 2020 version of "Second Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc," though the theoretical calculation was notably higher than the measured value of ΔH_{ttd}.[43] The heat capacity equation available in literature for UCl_3 is given by equation 5 where T is the temperature in K and the coefficients for the fit are provided in Table 3.

$$C_P = a + b * T + c * T^2 + \frac{E}{T^2} + jT^3 \qquad \text{Eq. 5}$$

Table 3. Heat Capacity equation coefficients for solid UCl_3 from tabulated uranium compound data.[43]

Coefficient	Value for Solid UCl_3 (298-1700 K)
a	84.0180
b	-3.47320×10^{-3}
c	3.61300×10^{-6}
e	-7.98900×10^{4}
j	0

The integral heat capacity of each of the pure compounds was calculated by integrating the respective heat capacity equations (eq 4 and 5) with the respective coefficients (Table 2 and Table 3) from room temperature to the calorimeter temperature. These calculated integral heat capacity values, in this case are equal to the theoretical ΔH_{ttd}, for all three pure compounds were recorded in Table 4 with the measured values.

Table 4. Theoretically calculated enthalpy of TTD of pure components compared to measured enthalpy of TTD. All error is reported in two standard deviations of the mean (2σ). The numbers in parenthesis denote the number of drops per sample.

	Nickel	NaCl	UCl_3
Room Temperature (K)	299 ± 4	296.5 ± 0.2	296.5 ± 0.3
Calorimeter Temperature (K)	1064.6 ± 0.2	1064.72 ± 0.02	1064.61 ± 0.01
Theoretical ΔH_{ttd} (kJ mol^{-1})	24.2*	44.2*	85.3**
Measured ΔH_{ttd} (kJ mol^{-1})	24.1 ± 0.3 (12)	44 ± 3 (4)	79 ± 5 (6)

*Integrated NIST Chemistry Webbook Shomate equation (equation 4)[14]
**Integrated heat capacity fitting from "Second Update on the Chemical Thermodynamics of U, Np, Pu, Am, and Tc" (equation 5)[43]

The theoretical ΔH_{ttd} were within error of the measurements for both pure Ni and NaCl, showing the measurements align well with literature. However, compared to the measured value of ΔH_{ttd} for the pure UCl_3, the theoretically calculated value is significantly larger and not within the error of the measurement. A description of the methods used to produce the heat capacity equation and fitting coefficients for the pure solid UCl_3 is missing from the source literature. The observed discrepancy for the UCl_3 could also be due to the lack of available thermodynamic data, a challenge nonexistent to the nickel and sodium chloride compounds.

The ΔH_{ttd} of the UCl_3-NaCl eutectic (34-66 mol%) was also measured via high temperature transpose drop calorimetry as shown in Table 5. The liquid heat capacity of the eutectic must be measured via differential scanning calorimetry before the enthalpy of mixing can be extracted from the total ΔH_{ttd}. Understanding the solid heat capacity of the eutectic and the formation of any other potential intermediate compounds that are currently under debate in literature will also aid in deconvoluting the measured ΔH_{ttd}. Further drop calorimetry on non-eutectic mixtures in this system will also provide necessary information for understanding the enthalpy of mixing in the binary UCl_3-NaCl system.

Table 5. High-temperature transposed-temperature drop-calorimetric results of the endmember and eutectic compositions of the UCl_3-NaCl system. All error is reported as two standard deviations of the mean (2σ). The numbers in parenthesis denote the number of drops per sample.

Mol fraction UCl_3	Mol fraction NaCl	T_{Room} (K)	$T_{Calorimeter}$ (K)	Experimental ΔH_{ttd} (kJ mol^{-1})
0	1	296.5 ± 0.2	1064.72 ± 0.02	$44 \pm 3(4)$
0.344 ± 0.004	0.656 ± 0.004	296.5 ± 0.3	1064.53 ± 0.03	$92 \pm 5(4)$
1	0	296.5 ± 0.3	1064.61 ± 0.01	$79 \pm 5(6)$

2.4 Future directions

Extracting the enthalpy of mixing (ΔH_{mix}) from the high temperature transpose drop measurements will require ΔH_{ttd} measurements of more molar compositions of the UCl_3-NaCl system as well as DSC measurements of the compositions of interest to determine the enthalpy of fusion (ΔH_{fus}) and integral heat capacities of the liquid mixtures. DSC will also verify the existence of an intermediate compound; formation of any intermediate compounds would have their own enthalpy response that would need to be considered when extracting ΔH_{mix} from ΔH_{ttd} of the different compositions. Further TTD measurements will be performed on different molar compositions of UCl_3-NaCl system as well as a comparison TTD experiment of a pre-melted, or cast, eutectic mixture that will aid in deconvolution of the ΔH_{ttd}.

3 Conclusions

The high temperature transpose drop calorimetry (ΔH_{ttd}) work performed at LANL for the MSR Campaign verified the methodology for radioactive and air-sensitive materials. This work provided opportunities to improve and streamline the TTD experimental procedure while still collecting data crucial to the molten salt reactor community. Measurements of the solid integral heat capacity, or enthalpic increment ($\Delta H_{T\text{-}298.15}$), for the eutectic $PuCl_3$-NaCl as well as the liquid enthalpic increment ($\Delta H_{T\text{-}726}$) were found to be in good agreement with existing DSC measurements from INL and indicated that the liquid heat capacity of the $PuCl_3$-NaCl is not dependent on temperature. Using the enthalpic increments and enthalpy of fusion for the thermochemical reaction of the eutectic $PuCl_3$-NaCl available allowed for the extraction of the excess heat capacity (C_p^{ex}) that was then used to determine the enthalpy of mixing (ΔH_{mix}). Future ΔH_{ttd} work on the UCl_3-NaCl binary system will allow for deconvolution of the eutectic data collected during this reporting period, including determination of C_p^{ex} and ΔH_{mix}. Experimentally determining the enthalpy of mixing for the UCl_3-NaCl system at different molar compositions will provide important data that will aid modelling efforts including MD simulations and CALPHAD methods, providing accurate and precise phase diagrams.

With the successful completion of renovations at the LANL Plutonium Science Laboratory (PluS Lab), the facility will begin a broad program of Pu fundamental research in FY26. Among these activities will be Pu chloride and fluoride thermochemical analysis and phase transition determination via DSC. These efforts will be complemented by high-temperature transpose drop calorimetry, together yielding critical experimental data to support reactor concepts considering Pu fuel salts.

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