

Molten Salt for Molten Salt Reactors (MS4MSRs)

A THERMODYNAMIC EXPLORATION AND CHARACTERISATION OF
ALTERNATIVE NUCLEAR MOLTEN FUEL SALT SYSTEMS

FINDLAY, JOSHUA

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School of Engineering, Lancaster University
United Kingdom

Abstract

This thesis presents a comprehensive thermodynamic investigation of alternative molten salt systems for use in both thermal- and fast-spectrum molten salt reactors (MSRs). The work integrates new experimental data with advanced thermodynamic modelling to establish a consistent and validated database for both fluoride- and chloride-based fuel salts, many of which had not been previously examined.

A series of Differential Scanning Calorimetry (DSC) experiments were conducted to determine phase equilibria, eutectic compositions, and enthalpies of mixing in key binary and ternary systems. A custom hermetically sealable, high-sensitivity crucible was designed and developed to enable accurate DSC measurements of volatile and corrosive salt systems – representing a novel technical contribution of this work. These data formed the foundation for thermodynamic optimizations using Gibbs energy functions, allowing reliable prediction of phase equilibria, melting points and respective compositions, redox potentials, chemical activities, vapor pressure and other excess thermodynamic properties relevant to reactor operation and safety.

The thesis follows a hybrid structure comprising three peer-reviewed publications and supporting chapters. The RbCl-CeCl_3 and RbF-CeF_3 systems were experimentally investigated and modelled to establish reliable surrogates for actinide chlorides and fluorides (PuCl_3 and PuF_3 , respectively). The RbCl-UCl_4 system was measured for the first time using DSC, providing entirely novel experimental data, while the RbF-UF_4 system was re-measured to validate historical data and generate additional thermodynamic property information. The $\text{CeF}_3\text{-UF}_4$ and $\text{CeCl}_3\text{-UCl}_4$ surrogate systems were measured for the first time using DSC, providing novel experimental data and enabling calculation of new thermodynamic properties. The systems were subsequently modelled as solid solutions incorporating lattice vacancies, which better reflect real crystal behaviour than interstitial substitution, improving both reliability and predictive accuracy. Building upon these binary descriptions, new ternary systems (RbF-

$\text{PuF}_3\text{-UF}_4$ and $\text{RbCl-PuCl}_3\text{-UCl}_4$) were constructed and analysed to assess the thermodynamic stability and reactor suitability of Rb-based salts compared to traditional Oak Ridge National Laboratory (ORNL) LiF-BeF_2 containing mixtures.

Collectively, this work provides the novel integrated experimental–computational framework linking measured thermodynamic data with predictive modelling across multiple halide systems. The resulting database and modelled liquid solutions significantly enhance the understanding of MSR-relevant salts and supports the identification of optimized compositions that balance critical properties, laying the groundwork for Rb containing alternative fuel salts.

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“I am one of those who think like Nobel, that humanity will draw more good than evil from new discoveries” – Marie Curie

Author's Declaration

I declare that the work presented in this thesis is my own, except where otherwise stated. Any sources used have been properly acknowledged. This thesis has not been submitted for any other degree or qualification at this or any other institution.

Chapter 1: Introduction

One of the greatest challenges facing humanity today is sustaining a growing global population, projected to increase until at least 2100, while drastically reducing CO₂ emissions [1]. The majority of these emissions arise from the combustion of fossil fuels, and persistent energy inequality continues to hinder economic development in many regions. Ensuring adequate energy supply - and expanding access in developing regions - in an environmentally responsible manner therefore remains one of the defining problems of this century.

Among all available energy sources, nuclear power stands out as uniquely capable of addressing these challenges. It provides constant, reliable, 24/7 baseload energy with virtually zero carbon emissions. Unlike other clean energy systems that have made tremendous strides in progress, nuclear is geographically flexible, does not rely on weather and offers strong energy security with a minimal land footprint. Its exceptional energy density - where a single fission event releases ~200 MeV, releases roughly 20 million times more energy than the combustion of one methane molecule (~9 eV) - means far less fuel, raw ore and material extraction are required to meet energy needs. Energy density is a critical consideration in assessing energy logistics. While nuclear power also requires fuel handling and transport infrastructure, the scale is incomparable to that of fossil fuels. A 1 GW fossil-fuel plant requires oil and gas refineries, along with extensive networks of pipelines, ships, and rail systems. By contrast, a nuclear plant of similar size can run for years on fuel stockpiled in an area smaller than a typical car park, though it still needs initial ore mining, complex chemical conversion and enrichment. In terms of volume, the process flow rates for nuclear fuel are orders of magnitude lower.

As global energy demand continues to rise, it is important to acknowledge that approximately 85% of total energy consumption remains dedicated to generating heat for industrial and chemical processes essential to modern society, rather than electricity [2]. At the same time, renewable energy technologies have made tremendous progress and can supply large-scale electricity with very low emissions, particularly when supported by storage, demand management, or grid

interconnections. Renewable energy installations have grown remarkably in recent years; however, when considering total capacity additions globally, fossil fuels remain dominant, outpacing the net growth of renewables. A balanced energy strategy recognises the complementary strengths of nuclear with other technologies in achieving low-carbon, reliable electricity systems while minimising fossil fuel dependence.

With specific reactor types of unparalleled ability to deliver both electricity and high-temperature process heat, nuclear energy stands as one of the most practical and scalable pathways to achieving sustainable energy security and deep decarbonisation. Beyond electricity and high-temperature heat, nuclear power can also utilise low-grade waste heat for district heating. This heat is normally rejected in the condenser - via cooling towers or bodies of water - to convert the exhaust steam back into water and complete the Rankine thermodynamic cycle in electricity production. For example, China's Haiyang Nuclear Power Plant is expected to heat the entire city of Haiyang (population ~670,000) [3], while Switzerland's Beznau plant has provided district heating for decades [4].

Looking ahead, global efforts must focus on expanding these proven, low-carbon sources while advancing new generations of nuclear reactor technologies suited to regional demands. Although progress in nuclear development slowed in recent years due to rising upfront capital costs, extended construction timelines and safety concerns due to recent accidents [5], these challenges are limited to certain countries, financing [6] and specific reactor types, underscoring that there remains vast potential for innovation and improvement.

1.1 Revisiting Molten Salt Reactors: Innovation and Potential

Originally conceived to power long-range bombers capable of remaining airborne for extended periods without refuelling, the Aircraft Reactor Experiment (ARE) was conducted in 1954 at Oak Ridge National Laboratory (ORNL) in the United States [7]. Its goal was to evaluate the feasibility of using a molten salt fuel to generate the high-temperature heat required to drive turbojet engines. At the time, other solid-fuel reactor concepts were also under development; however, Pressurized Water

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Reactors (PWRs), operating at roughly 573 K and requiring heavy, high-pressure vessels were unsuitable for aviation applications due to their weight and insufficient outlet temperatures for turbine propulsion. The ARE employed a NaF-ZrF₄-UF₄ molten salt fuel mixture, achieved criticality, and successfully produced power at temperatures up to 1123 K before the program was ultimately discontinued. This specific mixture was used primarily due to its moderately low melting point of 838 K and neutronic properties, since the non-uranium constituents in the salt have low neutron absorption cross-section in the thermal spectrum.

Led by Alvin Weinberg at ORNL during the 1960-70s, Weinberg championed the adoption of molten salt reactors for civilian energy applications. The Molten Salt Reactor Experiment (MSRE) [8] was designed, constructed, and operated for a total of 2500 hours between 1964 and 1969. This small prototype was a graphite-moderated, thermal-spectrum reactor using a molten salt mixture of ⁷LiF-BeF₂-ZrF₄-UF₄ (65.0 - 29.1 - 5.0 - 0.9 mol%) at 923 K. This mixture was selected for its lower melting point of 763 K and its favourable neutronic properties, with the non-uranium constituents exhibiting low neutron absorption in the thermal spectrum, making it superior to the fuel salt used in the ARE. Initially, the uranium in the salt was enriched to 33% ²³⁵U, and the reactor was later fuelled with ²³³U bred from ²³²Th irradiated in earlier reactors in Idaho and New York. Weinberg and his team conducted an extensive array of studies exploring alternative salt mixtures, salt chemistry, and the compatibility and degradation of structural materials. Although some unresolved challenges remained, vast operating experience and knowledge was gained from this program.

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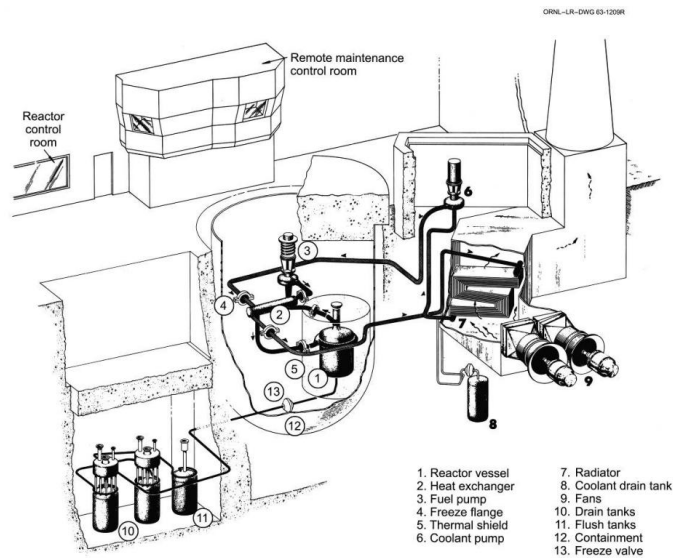


Fig 1. 1: Schematic of the MSRE with labelled components.

Building on Weinberg's work, the conceptual Molten Salt Breeder Reactor (MSBR) at ORNL became the next major research effort, aimed at developing a 1000 MW_{th} reactor using a ${}^7\text{LiF}\text{-BeF}_2\text{-ThF}_4\text{-UF}_4$ fuel salt operating at 978 K [9]. This program was far more extensive than the MSRE, employing forced-convection loops to study how molten salt interacts with structural materials under flow and thermal gradients. The team also investigated chemical processing systems to clean and treat the salt and explored advanced power conversion cycles. The program was officially terminated in 1976 for a combination of reasons, primarily political. U.S. policy shifted toward continued development of proven PWR technology for naval propulsion and scaling these reactor types for civilian electricity, as well as fast liquid-metal breeder reactors. Initially, breeders were considered essential due to concerns about uranium scarcity, but by the mid-1970s it was becoming clear that uranium reserves were far more abundant than previously anticipated, and by the early-1980s, the breeder program was terminated.

Nuclear reactor development has progressed through four generations. Generation I reactors, built in the 1950s and 1960s, were early prototypes such as the Shippingport and Magnox designs, focused on demonstrating the feasibility of nuclear power, but with relatively low efficiency and limited safety systems. Generation II reactors, developed from the 1970s to 1990s, brought commercial

standardization, higher thermal efficiency, longer operational lifetimes, and improved safety, exemplified by PWRs, BWRs, and CANDU reactors. Generation III and III+ designs further enhanced these features, incorporating passive safety systems, extended lifetimes, and more efficient fuel use, with examples including the AP1000, EPR, and Advanced CANDU. Looking ahead, Generation IV reactors, still under development, aim to achieve greater sustainability, inherent safety, and efficiency through advanced concepts such as fast reactors, molten salt reactors, high-temperature gas reactors, and lead-cooled systems, with goals including fuel recycling, minimal waste, and efficiencies exceeding 45%.

In recent years, there has been a resurgence of interest in molten salt reactor (MSR) technology, driven by growing energy demands and the need for low-carbon, sustainable energy sources that meet multiple criteria. To advance the development of the fourth generation of nuclear reactors, the Generation IV International Forum (Gen-IV) [10] was established as an international collaborative effort. Gen-IV reactors are required to meet the following objectives:

- **Sustainability:** Gen-IV nuclear systems aim to provide clean energy, ensure long-term fuel availability, maximize fuel utilisation, and minimize radiotoxic waste, particularly reducing the burden of long-term stewardship.
- **Economics:** These systems should offer clear life-cycle cost advantages over other energy sources while maintaining financial risks comparable to conventional energy projects.
- **Safety & Reliability:** Gen-IV reactors are designed to achieve exceptional safety and reliability, with a very low likelihood of core damage and no need for off-site emergency response.
- **Proliferation Resistance & Physical Protection:** Gen-IV systems must be highly unattractive for diversion or theft of weapons-usable materials and provide robust protection against acts of terrorism.

The potential for MSRs to address these considerations, but with the key difference against other Gen-IV designs, is that MSRs are unique in that they have liquid fuel.

Unlike their solid-fuelled counterparts which have typically either uranium metallic fuel or solid uranium oxide fuel.

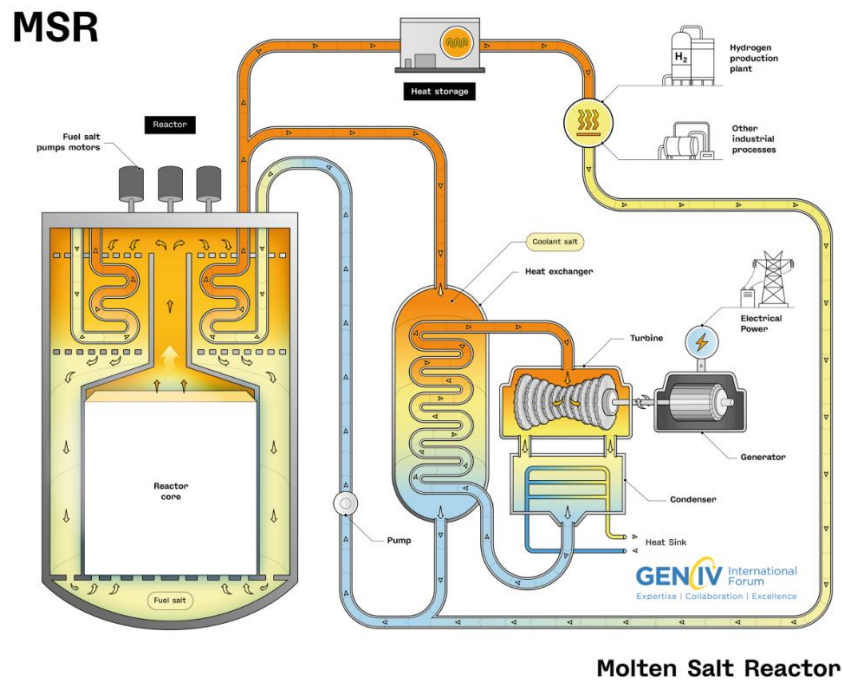


Fig. 1. 2: Schematic of the Gen-IV example MSR layout [11].

The advantages of molten salt reactor (MSR) technology are extensive; however, several technical and practical challenges still limit their large-scale deployment and commercialisation. The key advantages that distinguish MSRs from conventional pressurised water reactors (PWRs) and other Generation IV reactor concepts are summarised below.

- **Inherent safety:** Molten salt fuel is effectively meltdown-proof, with normal operation consisting of the fuel already being in a molten state [12]. Molten salts allow for low operating pressures, and major fission products of concern - normally highly volatile in solid fuel; ^{131}I , ^{137}Cs and ^{90}Sr - remain soluble in the molten fuel salt, significantly mitigating risk of radiological release in major accident scenarios [13].
- **High-temperature operation >773 K:** Temperatures surpass conventional PWR limits ($\sim 573\text{ K}$), enabling higher thermal efficiency (over 40%) in a steam Rankine

cycle and the provision of process heat for industrial applications [14]. Additionally, MSRs can make use of conventional high-temperature steam turbines from the fossil-fuel sector, avoiding the need for the specialised low-enthalpy designs used in PWRs.

- **Flexible fuel cycles:** Supports breeding of thorium-232 to uranium-233 and uranium-238 to plutonium-239, vastly enhancing fuel sustainability and ensuring growing energy requirements are met far into the future [15], [11].
- **Online refuelling and long fuel life:** By avoiding solid fuel pin assemblies and cladding, molten salt reactors eliminate the need for complex fuel assembly reshuffling during refuelling, enabling continuous operation. The liquid, homogeneous fuel allows fissile material to be added as it is consumed and ensures thorough mixing, resulting in longer core residence and minimal out-of-core periods. This eliminates recasting and precision fabrication of solid fuel pellets, accelerating breeding and reducing doubling times [16].
- **Reduced radiotoxicity:** Fast neutron molten salt reactors can produce significantly less long-lived waste, as higher actinides (with long half-lives) remain in the fuel and are eventually fissioned. The most radioactive components are the fission product isotopes (with short half-lives), which are extracted and decay within approximately 300 years rather than hundreds of thousands, greatly reducing the requirements for deep geological repositories (DGRs) [17].
- **Fission product management:** Fission products, including prominent neutron poison; xenon, can be more readily stripped from the liquid fuel, enabling better reactor control and neutron economy. Removal of other fission products could result reduced decay heat requirements and medical isotope extraction [18].
- **Load-following capability:** Thermal expansion of the fuel results in increased neutron leakage and thus a strong negative temperature coefficient. In addition, MSRs coupled with high temperature molten salt thermal storage allows entire power plants to rapidly adjust according to demand or to compliment variable renewables [12].

- **Neutronics advantages:** Continuous removal of fission products, combined with the minimal use of solid structural components within the MSR core, improves neutron economy, enabling more efficient breeding and fuel utilisation [15], [19].
- **Modular and SMR potential:** Designs can be scaled or deployed in modular configurations for flexible power deployment and reducing large upfront capital normally associated with modern large nuclear plant builds [20].
- **Material resilience:** Unlike conventional solid oxide fuels that experience swelling, cracking, and structural degradation as fission proceeds [21], molten salt fuels composed of fluoride or chloride salts in their liquid phase exhibit exceptional chemical and physical resilience to radiation damage, thereby minimising material degradation and reducing the frequency of fuel maintenance or replacement.
- **Drain tank and reactor geometry flexibility:** Liquid fuel also allows for a wider range of reactor geometries to achieve criticality and operate in different modes, including breeder, burner, or converter configurations. Moreover, molten salt reactors can achieve passive fail-safe shutdown without operator intervention or active pumping systems. In the event of overheating, gravity can drain the fuel into subcritical storage tanks where it passively cools, preventing re-criticality and safely dissipating decay heat [12].

1.2 Remaining challenges

The MSRE and the MSBR programme made significant contributions to molten salt science and technology, yet several challenges remained unresolved at the conclusion of these experiments. Issues such as policy and economic support, continuous reprocessing (via electro-pyroprocessing, liquid-phase immiscibility gaps, fluorination/chlorination and distillation), and management of noble fission-product gases fall outside the scope of this work. However, technical challenges like tritium production and containment from lithium-containing salts, corrosion and alloy compatibility, and the persistent Cr-leaching and tellurium-induced

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intergranular cracking of Hastelloy-N remain highly relevant [22]. The MSRE also experienced graphite moderator degradation [23], another key concern, but can be partially assessed and addressed through thermodynamic evaluation, which forms another area of this study. Much of the historical research concentrated on LiF-BeF₂ (FLiBe) salt mixtures, yet a broad range of potential salt compositions remains largely unexplored. The number of viable candidates is ultimately constrained by thermodynamic stability, chemical compatibility, and neutronic suitability, but certain adjustments, such as removing LiF from the fuel matrix can mitigate issues like tritium production entirely.

FLiBe was historically favoured for its exceptionally low neutron absorption cross-section, a key requirement in thermal-neutron breeder MSRs [24], where the limited excess neutrons generated per ²³³U fission necessitate careful neutron economy to enable breeding. These constraints strongly influenced both fuel and reactor design, particularly for breeding objectives. In contrast, contemporary MSR development generally focuses on gaining operational experience and advancing technical knowledge rather than immediate breeding performance. The Thorium Molten Salt Reactor – Liquid Fuel 1 (TMSR-LR1) in China [25], building on from ORNL's MSRE released open access documents is also using UF₄ in FLiBe fuel matrix, but does not represent an exception, as thorium breeding remains one of their key goals, although detailed information on its operation remains limited in the publicly available literature. This shift opens the door to alternative salt compositions, allowing the exploration of materials that were previously overlooked, while still satisfying the core requirements of safety, stability, and neutronic performance.

Other challenges that must be addressed for MSRs to achieve successful licensing and operation include ensuring the high reliability of fuel pumps and designing systems that allow for straightforward maintenance. Salt freezing in unintended regions could restrict flow and create operational difficulties. It remains uncertain whether frozen regions will naturally remelt if left untreated or whether they could lead to further complications. Thermal gradients within the reactor core and primary heat exchanger are also critical to power generation. The solubility behaviour of

various fission product gases under these gradients is not yet well understood, raising concerns about the possible deposition of fission products along colder sections of the system. Finally, the management of insoluble noble metal fission products poses another challenge. These colloidal particles may accumulate in low-velocity zones and could require removal through mechanical filtration, cold traps, or flow control methods. All of these factors are noteworthy, as the alternative fuel systems explored in this work can exhibit highly different chemical and thermodynamics properties that influence such phenomena. However, these considerations lie outside the direct scope of this thesis.

1.3 Importance of fuel chemistry and thermodynamics - Rationale and Objectives of this PhD Thesis

Thermodynamic modelling provides a powerful means of describing the solution behaviour of molten salts. Ionic liquids at elevated temperatures can exhibit significant deviations from ideal behaviour due to strong ion-ion interactions. While modelling alone cannot fully capture all thermo-physical properties, when integrated with experimental data and system-specific considerations, it enables accurate prediction of key parameters such as phase equilibria, melting points, heat capacities, vapour pressures, chemical activities, and redox potentials - all of which are critical for identifying suitable MSR fuel compositions.

In this work, RbF- and RbCl-based systems are investigated, in some cases for the first time, in combination with actinide-bearing salts for thermodynamic optimisation. Fluoride salts are generally favoured for thermal-spectrum MSRs, while chlorides are preferred in fast-spectrum designs due to their differing neutron absorption characteristics. RbF and RbCl, when used as carrier salts with uranium and plutonium halides, remain relatively underexplored but show promise as alternative fuel matrices for advanced molten salt reactor concepts. While lighter alkali-metal ions in halide salts, such as Li^+ , Na^+ and K^+ , are viable due to their low neutron absorption cross sections, they have already been extensively studied with uranium halides at fixed halide composition, for example NaCl-UCl_3 and LiF-UF_4 . In contrast, Rb^+ also exhibits a low neutron absorption cross section but can form

systems with lower eutectic melting points, often featuring multiple eutectics, which may enable higher fissile component loading. Other salts face limitations: CsF and CsCl have high neutron absorption, while PbCl_2 is radiologically unstable and prone to radiolysis, forming PbCl_4 , a highly volatile compound with a boiling point of 323 K. There are many types and classifications of MSR. In this work, the fuel - fissile components such as uranium or plutonium – itself is a salt, dissolved within the fuel matrix. Other MSR types do not necessarily use this fuel configuration, so for clarity, the different types are illustrated in **Fig. 1.3** below.

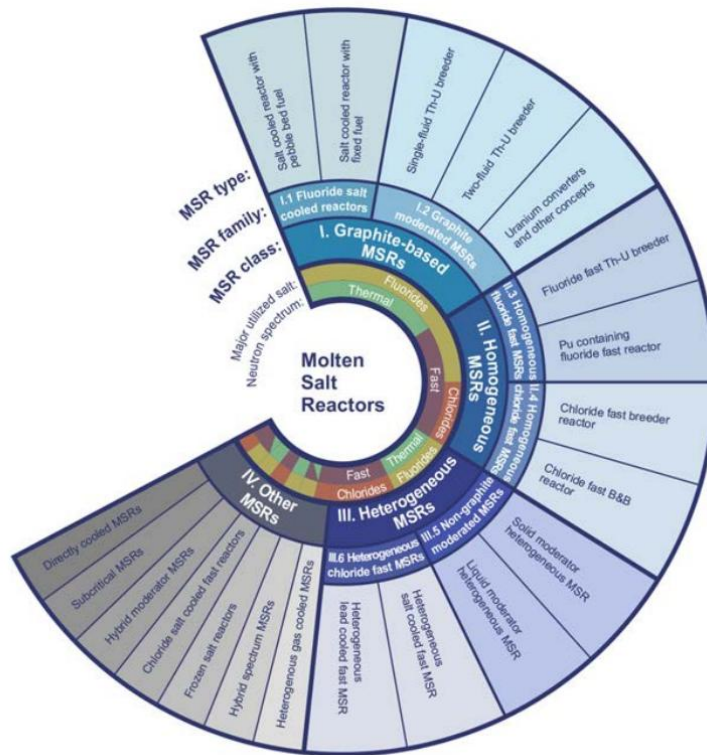


Fig. 1. 3: Classification of MSRs as a circular chart [26].

Certain thermo-physical properties, including viscosity and density, cannot be precisely determined through thermodynamic modelling alone. However, these are closely linked to the degree of short-range ordering (SRO) within the molten salt, a relationship examined in later chapters. Differential Scanning Calorimetry (DSC) measurements are used to construct phase diagrams, forming the experimental foundation for thermodynamic optimisation. The calculations are carried out using the CALculation of PHase Diagrams (CALPHAD) methodology [27] and the Modified

Quasichemical Model in the Quadruplet Approximation (MQMQA) [28], implemented in the thermochemical software package FactSage (Version 8.3).

The study first examines binary systems (RbCl-PuCl_3 and RbF-UF_4) before extending the analysis to ternary systems such as $\text{RbF-PuF}_3\text{-UF}_4$. These models include detailed thermodynamic descriptions of all relevant solid, solid-solution, and liquid phases, allowing direct comparison with literature data. The systems examined are not necessarily intended to represent beginning-of-life (BOL) MSR fuels, they may act as $\text{RbF-PuF}_3\text{-UF}_4$ -containing sub-systems of more complex mixtures (e.g., $\text{RbF-CaF}_2\text{-PuF}_3\text{-UF}_4$) that may offer possible improved properties such as reduced eutectic melting points, lower neutronic absorption cross-sections, higher fissile concentrations, or greater solubility for fission products – all of which would need further experimental validation in future works.

Vapour pressure calculations are not included at this stage, as priority is given to characterising the liquid phase to establish fundamental compatibility, given its role as the operational fuel medium. Once optimised, the models developed in FactSage can be used to calculate redox potentials and construct Ellingham-type diagrams, which provide valuable insight into the oxidising or reducing nature of fuel salts. Such analyses can help identify less corrosive mixtures and assess potential chemical interactions with reactor materials including graphite and various structural alloys. Addressing this aspect is crucial, as MSRs remain under scrutiny by critics for their corrosive properties, yet few recent studies consider it in detail from a thermodynamic perspective. By correctly integrating FactSage, this work illustrates the software's capability to provide a robust and insightful analysis.

All thermodynamic modelling presented in this thesis employs the MQMQA framework. A key innovation of this work lies in representing the liquid phase as a function of the concentrations of complex ionic species within the melt, rather than as a function of the mole fraction of a single end-member component (e.g., UF_4). This approach involves manually 'destabilising' pure actinide salt components (such as UF_4) in the FactSage software and modelling the actinide salts as mixtures of actinide complexes that exhibit ordering at specific compositions - an effect also supported by various Raman spectroscopy studies. The methodology follows

techniques originally developed at the Centre for Research in Computational Thermochemistry (CRCT), Polytechnique Montréal, to improve model reliability for industrial molten salt aluminium smelting [29], [30]. These models can be further refined by assigning electrochemical properties to the complexes - crucial for optimising industrial electro-arcing processes - as well as other physicochemical properties such as density [31] and viscosity [32], all associated with the degree of SRO. Although beyond the scope of this thesis, this strategy could be applied in future work to the electrochemical processing of MSR back-end fuel cycles and is therefore worth noting.

Traditional models typically relate the Gibbs energy of the liquid to the concentration of one end-member component. While this approach can yield satisfactory binary phase diagrams, it becomes increasingly unreliable as system complexity increases to ternary and higher-order compositions. This is because certain molten salt systems, particularly those containing actinides, deviate significantly from ideal solution behaviour, as they do not exhibit random mixing of independent ionic species. Instead, they form distinct SRO clusters or complexes - also confirmed by many Raman spectroscopy studies.

By modelling the liquid phase through Gibbs energy functions associated with these complexes rather than with conventional end-member components, the robustness and predictive accuracy of the thermodynamic models are substantially improved. This methodology ensures reliable estimation of key thermodynamic properties, including phase equilibria, melting points, heat capacities, vapour pressures, chemical activities, and redox potentials which form the analytical foundation of this thesis.

1.4 Thesis structure and chapters outline

The scope of this thesis is to provide a comprehensive thermodynamic description of alternative fuel systems for molten salt reactors (MSRs), encompassing both fluoride-based salts for thermal-spectrum MSRs and chloride-based salts for molten salt fast reactors (MSFRs). Several of these systems have not been previously investigated and warrant further exploration. The approach adopted in

this work combines experimental Differential Scanning Calorimetry (DSC) measurements with thermodynamic modelling. New experimental data were obtained to expand the existing knowledge of fundamental binary systems, from which a consistent thermodynamic database incorporating all key systems was developed.

Based on the experimental results and subsequent calculations, the primary objective is to identify eutectic fuel compositions within binary and ternary systems suitable for reactor applications, and to analyse their associated thermodynamic properties. Many salt systems remain unexplored, and their eutectic compositions have yet to be determined; however, identifying these is crucial for MSR operation, as multiple eutectics can occur at different temperatures and compositions, significantly influencing reactor performance. The main body of this thesis is organised into three parts, as schematically illustrated in **Figure 1.4**.

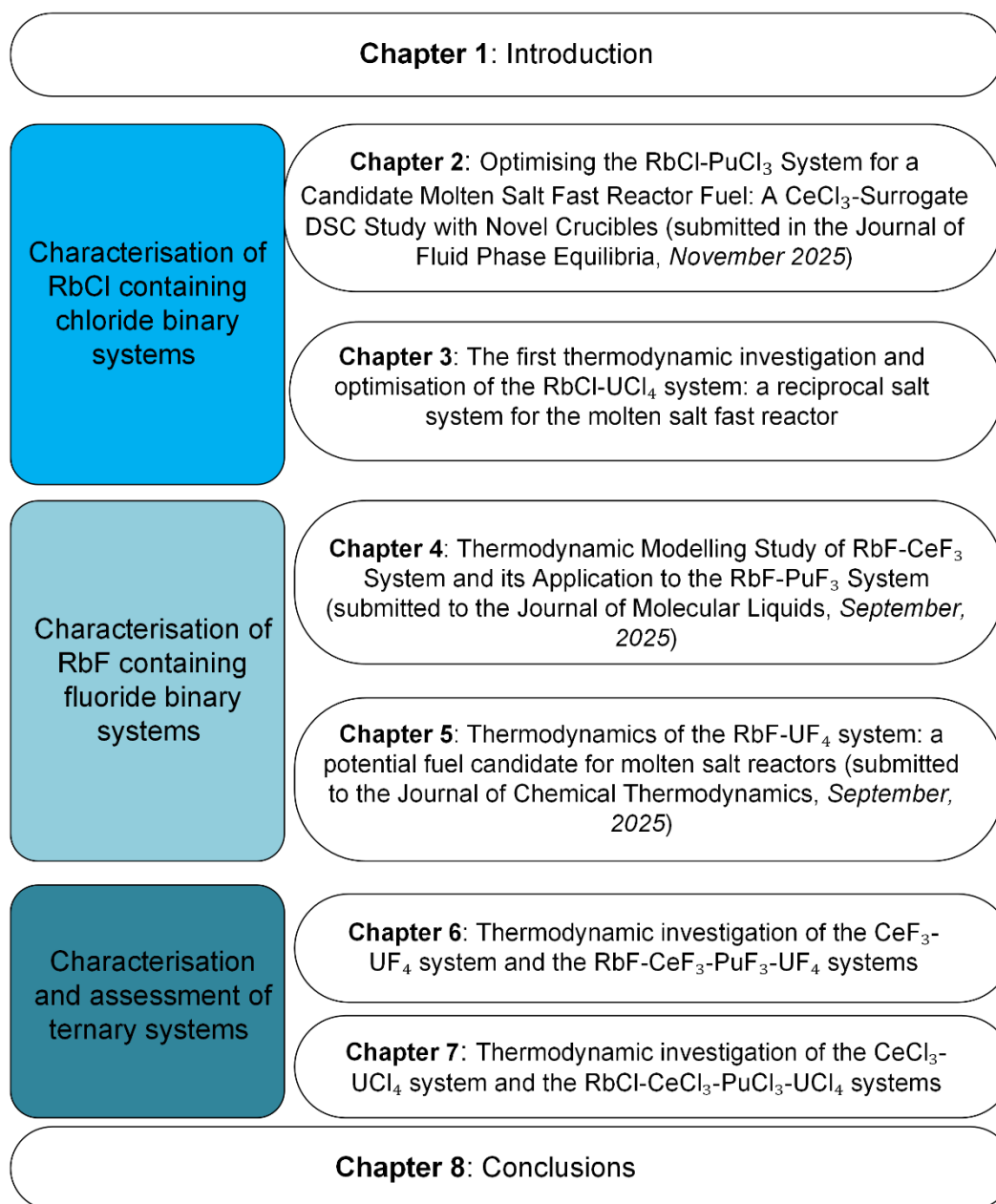


Fig. 1. 4: Schematic of this thesis content.

The Differential Scanning Calorimetry (DSC) experiments for the uranium-based systems were conducted using a Hitachi STA-7200 series instrument. The crucible and sample combined were limited to a maximum mass of 400 mg and a diameter of 5 mm. It was soon recognised that a hermetically sealable crucible was essential, as even minor vaporisation in an unsealed crucible led to compositional shifts, rendering the recorded DSC thermal events unreliable. However, no commercially

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available crucible met the necessary requirements: hermetically sealable, non-corrosive, capable of maintaining good thermal contact with the DSC holder, lightweight (under 380 mg, assuming a 20 mg salt sample), and with adequate thermal conductivity. Consequently, a high-sensitivity custom crucible was designed and developed as part of the novel contributions of this work.

The thesis adopts a hybrid format consisting of three publications [33], [34] and [35] presented as Chapters 2, 4, and 5, along with three conventional chapters. Each chapter includes a literature review, methodology, results and discussion, and conclusions. A final chapter provides an overarching conclusion, summarising the work and proposing future research directions, as this field is still emerging with numerous unexplored salt systems, especially ternary and higher-order compositions.

In Chapter 2, the RbCl-CeCl_3 system was examined over a range of compositions using the DSC to validate the novel crucible design and assess phase equilibria against literature data obtained via Differential Thermal Analysis (DTA). Following experimental validation, the RbCl-CeCl_3 system was thermodynamically optimised using Gibbs energy functions associated with the complexes present in the melt. Since CeCl_3 serves as a reliable and accessible surrogate for PuCl_3 , the RbCl-PuCl_3 system was subsequently remodelled using the same approach.

In Chapter 3, the phase equilibria of the RbCl-UCl_4 system were measured by DSC for the first time and subsequently optimised, with excess properties, activities and redox potentials calculated at the eutectic compositions.

Chapter 4 follows a similar approach to Chapter 2, employing CeF_3 as a surrogate for PuF_3 in the RbF-PuF_3 system. This approach is expected to yield far more reliable results than previous modelling efforts by other authors, such as those using LaF_3 as a surrogate for PuF_3 .

In Chapter 5, the phase equilibria of the RbF-UF_4 system were measured by DSC, validating decades-old data originally obtained at ORNL. The system was then optimised, and additional thermodynamic properties such as excess heat capacity and redox potential were calculated and demonstrated.

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Finally, the binary systems developed in Chapters 2–5, with fluoride and chloride systems treated separately, were used in Chapters 6 and 7 to construct and analyse newly developed ternary systems. The resulting properties were compared and discussed in depth, focusing on how the incorporation of RbCl and RbF affects thermodynamic stability, redox potential, and overall reactor suitability. These findings highlight the potential of Rb-based salt systems as potential alternative fuel candidates to those originally studied at ORNL, where LiF-BeF₂ mixtures were the primary focus.

Chapter 2: Optimising the RbCl-PuCl₃ system for a candidate molten salt fast reactor Fuel: A CeCl₃-surrogate DSC study with novel crucibles

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Joshua Findlay¹, Claude Degueldre¹, David Cheneler¹

¹ School of Engineering, Lancaster University, LA1 4YW, UK

2.1 Abstract

The binary chloride systems RbCl-CeCl₃ and RbCl-PuCl₃ are of relevance to molten salt fast reactor (MSFR) technology. In this study, CeCl₃ is employed as a non-radioactive surrogate for PuCl₃ in the RbCl system due to its analogous complex formation, closely matching phase behaviour, and relevance as a fission product, building on prior studies that validate the custom DSC crucible design for this work. The low-mass, high-sensitivity, corrosion-resistant, hermetically sealable differential scanning calorimetry (DSC) crucible enabled resolution of phase transitions within the system at elevated temperatures. RbCl as a carrier salt has received limited attention in the molten fuel salt literature. In this work, phase equilibria and the enthalpies of transitions for Rb_mM_nCl_{3n+m} intermediate compounds were measured by DSC and subsequently integrated into the thermodynamic model within the FactSage thermochemical software. The liquid phase was described using the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA), representing the first implementation of this model to incorporate two liquid complexes [MCl₄]⁻ and [MCl₆]³⁻ (M = Ce, Pu). This formulation enhances model reliability for increasingly complex systems, including fission product accumulation and higher-order RbCl-MCl₃ systems, where previously optimised models from other authors are not transferable. Raman spectroscopy has independently confirmed these species for M = La and Ce, both commonly used as surrogates for Pu. This study emphasises the role of RbCl containing systems, intermediate compounds and the liquid phase which influence phase

behaviour and the two eutectics, providing higher actinide solubility and potentially greater thermodynamic stability compared with lighter alkali metal chloride systems. The RbCl-PuCl₃ system could serve as a subsystem within ternary or higher-order systems in future investigations to achieve additional desirable properties. The newly optimised RbCl-PuCl₃ liquid solution was also analysed in an Ellingham diagram alongside other chloride salts and alloy components to assess redox potentials that may enhance corrosion resistance.

Keywords: RbCl-CeCl₃ system; RbCl-PuCl₃ system; Differential Scanning Calorimetry; Phase diagram; Molten salt reactor fuel

*Corresponding author: Joshua Findlay

2.2 Introduction

Molten salt reactors (MSRs) offer many potential benefits over Pressurised Water Reactors (PWRs), which remain the most widely deployed reactor technology today. MSRs were initially built and demonstrated by the U.S. in the 1950s and 60s, which is the foundation most of the current literature is based upon [36]. The main attractive features over conventional PWRs, include low operating pressures, high temperatures (>773 K), and inherent safety characteristics. These features have led to recognition of MSRs as a scalable replacement for fossil-fuel thermal plants, both for electricity generation and for providing direct heat to drive key industrial chemical processes [37]. The liquid fuel form also allows for continuous reprocessing and online removal of fission products, in contrast to solid-fuel systems, which require reactor shutdown, mechanical extraction, reprocessing, recasting, and refuelling. From an energy security perspective, these capabilities could improve neutron economy, enhance breeding potential, and most importantly, enable faster doubling times [38].

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This study focuses on chloride-based salt systems rather than fluorides for MSR fuel, as the higher atomic mass of chloride ions reduces neutron moderation. This property is essential for maintaining a fast neutron spectrum within the core, characteristic of Molten Salt Fast Reactors (MSFRs). In contrast, fluoride salt systems are better suited for thermal-spectrum MSRs, where neutron moderation is required to sustain criticality at lower fissile material concentrations.

Within fast-spectrum chloride systems, understanding the thermodynamic behaviour of actinide chlorides such as PuCl₃ is crucial for reactor design and modelling. However, due to its radiological hazards, cerium chloride (CeCl₃) is commonly employed as a surrogate for PuCl₃, owing to its similar chemical and physical properties, including comparable ionic radii, crystallographic structures, melting temperatures, and enthalpies of fusion. Additional thermodynamic data from related chloride systems - such as RbCl-CeCl₃, Alk-CeCl₃, and RbCl-LnCl₃ - are also used in this work to better model the liquid solution behaviour of RbCl-PuCl₃. Although Ce is radiologically inert, it remains a significant fission product, meaning its thermodynamic properties remain relevant for reactor operation and simulation.

In this work, CeCl₃ and PuCl₃ serve as one set of end-member components, while RbCl is chosen as the complementary end-member, despite receiving limited attention in previous molten salt thermodynamic studies. Historical efforts, such as the Molten Salt Reactor Experiment (MSRE) conducted in the 1960s by Weinberg's team, focused on thermal breeder designs utilizing FLiBe (⁶LiF-BeF₂) as the carrier salt. The choice of FLiBe was dictated by its exceptionally low thermal neutron absorption cross-sections, a property essential for breeding fissile material from thorium in a neutron-limited thermal spectrum.

Such constraints do not apply to MSFRs, where a fast neutron spectrum allows greater flexibility in salt selection. This opens the possibility of exploring alternative carrier salts, including heavier alkali chlorides such as RbCl, which may offer neutronic advantages by further minimising neutron moderation due to their higher atomic mass. Reducing moderation in MSFRs supports the objective of closing the

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nuclear fuel cycle, as fast neutrons are capable of efficiently fissioning long-lived higher actinides that are less reactive in thermal systems.

Therefore, the present work, focuses primarily on the thermodynamic assessment of these chloride systems. Establishing robust thermodynamic models and accurate phase-equilibria predictions is a prerequisite for determining the chemical compatibility and feasibility of candidate fuel salts during the early stages of material screening and reactor design.

RbCl-PuCl₃ emerges as a promising binary fuel salt system for MSFR startup. Unlike LiCl and NaCl, which each form a single eutectic with PuCl₃ (0.28 X at 734 K and 0.36 X at 726 K, respectively, where X is mol fraction of PuCl₃), RbCl forms two eutectics: 0.14 X at 903 K and 0.50 X at 777 K. KCl and RbCl mixtures with PuCl₃ both form two eutectics. KCl benefits from a low neutron absorption cross-section. However, in fast reactor systems, the higher atomic mass of RbCl reduces neutron moderation more effectively than KCl, so it remains a viable option. In contrast, CsCl has a significantly higher neutron absorption cross-section, which makes it unsuitable for MSR applications. KCl and RbCl may enable higher actinide solubility and greater flexibility in fuel formulation. Moreover, this system could serve as a basis for investigating more complex multicomponent fuels, such as KCl-RbCl-PuCl₃, which have not yet been explored. Such systems may contain several ternary eutectics with differing thermophysical and chemical properties. Some of these compositions could offer advantageous features - such as lower melting points comparable to LiCl-PuCl₃, reduced vapour pressure, improved corrosion resistance, or enhanced actinide and fission product solubility - though these potential benefits require further experimental validation.

This study investigates the RbCl-CeCl₃ binary phase diagram using Differential Scanning Calorimetry (DSC) with a newly developed, low-mass, high-sensitivity, hermetically sealable, low-cost crucible system, as no commercially available crucibles are suitable for this purpose. Data from two prior thermal analysis studies were also incorporated to validate the crucible design for future DSC studies. Engineered for high-temperature and corrosive environments, the ultra-lightweight

crucibles enabled precise measurement of phase transitions across a broad composition range. The results confirm and refine decades-old phase equilibria, thereby validating historical data and demonstrating the crucible's effectiveness for future high-accuracy thermodynamic studies of molten salts. Additionally, phase data for the RbCl-PuCl₃ system were modelled alongside RbCl-CeCl₃, highlighting the analogous behaviour of the two systems. Since ¹⁴⁴Ce is also a notable fission product, this investigation provides valuable data for incorporation into higher-order thermodynamic models of molten salt systems.

For the first time, the liquid phases of the RbCl-CeCl₃ and RbCl-PuCl₃ systems have been modelled to include complex ionic species such as [MCl₆]³⁻ and [MCl₄]⁻ (M = Ce, Pu), which are known to form at specific compositions. Their inclusion is supported by Raman spectroscopy studies [39], [40] confirming the existence of such species in closely analogous lanthanide chloride systems. Incorporating these complexes into thermodynamic modelling enhances model reliability and robustness as system complexity increases, for example, as fission products accumulate within the salt or in the development of ternary and higher-order models. This work provides a preliminary foundation for future studies applying this approach.

This improvement arises from assigning Gibbs energy functions to each complex species that tends to form and dominate at particular compositions within the binary system, rather than applying a Gibbs energy function to a homogeneous liquid solution based solely on the end-member components, such as PuCl₃.

2.3 Background and literature data

2.3.1 Phase diagram and prior studies

The study of phase diagrams and determination of the liquidus, solidus, eutectic and peritectic points are vital to successful operation of MSRs. The fuel component choice as well as the ratio of each component in the mixture must satisfy several parameters such as melting point for the lowest allowable operating temperature,

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adequate density to sustain/control fission rate, low viscosity for efficient fluid transport, heat capacity which allows the sizing of the vessel, neutronic performance, maximum allowable enrichment for the given actinide salt composition. As the fission reaction proceeds, the composition itself also varies and shifts.

If the salt composition is on the RbCl rich side and cooling occurs so that it reaches below the liquidus point, RbCl will begin to precipitate out of solution. This mechanism would create liquid solution now higher in composition of PuCl₃, thus accelerating the rate of fission, thereby increasing the heat produced. This phenomenon of how non-actinide solid components precipitate out of solution is not fully understood. It could be self-controlling due to the bulk liquid having higher concentration of the actinide components, resulting in an increased fission rate and therefore an increase in temperature which could re-melt the solidified RbCl.

Similarly, if the fuel composition is higher in the PuCl₃, the actinide salt would precipitate out first if cooling was reach below the liquidus. From there, multiple events could ensue, such as fissile components precipitating on the vessel walls and depending on the density of the solid fissile material relative to the bulk fuel salt, could rise or fall to the bottom of the vessel forming hot spots and possible uncontrolled criticality. The remaining fuel salt, containing less actinide would experience a decrease in the rate of fission, thus, cooling it even further, exposing risks of entire shutdown due to solidification. Another hypothesis would be that said hotspots would allow the PuCl₃ precipitates to re-melt into the bulk salt – maintaining self-control of reactivity.

The same can be said for understanding the chemical activity and vapour pressure of each component in the salt. Although the vapor pressure is very low in molten salt, vapor deposition in headspaces is still experienced in industrial practice such as concentrated solar plants using molten nitrate salt [41], therefore determination of the excess partial Gibbs terms allow a better understanding of the composition of vapour depositions that could occur during helium purging, processing or extraction of valuable fission products.

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Two prior investigations were performed on the RbCl-CeCl₃ binary system by Gromov [42] and Seifert [43]. In Gromov's work, the literature states that high purity RbCl was used, which is in good alignment with current literature, as their temperature of fusion of the RbCl was recorded at 995 K, yet it is not clear whether this is onset temperature or peak temperature. The CeCl₃ was prepared by reacting cerium carbonate with aqueous HCl solution in the presence of a six-fold excess of ammonium halide. This solution was then dried by gradual heating in a water bath and freed from ammonium halide by gradual heating in a vacuum. This preparation method proved to be inadequate as the temperature of fusion of CeCl₃ that was recorded was 1078 K, instead of 1090 K, which was recorded experimentally in this work – also consistent with I. Barin's [44] data within the Factsage FactPSBASE database. In Seifert's work, the text does not mention how RbCl was prepared, but anhydrous CeCl₃ was heated for one day under vacuum with a continuous stream of HCl and then heated to its melting point and subsequent cooling in an Ar stream.

Seifert et al. detect Differential Thermal Analysis (DTA) signals at 651 K, which combined with X-ray powder patterns, is identified as the temperature of formation of Rb₃CeCl₆ reaction from the reaction of RbCl and Rb₂CeCl₅. Gromov does not detect any thermal effects in these ranges. R. Benz's [45] work in the RbCl-PuCl₃ system, confirms Rb₃PuCl₆ polymorphic phase transition with microscopic examinations. L. Rycerz (1999) [46] measured the heat capacity of Rb₃MCl₆ (M = La, Ce, Pr, Nd) compounds demonstrated further evidence that Rb₃CeCl₆ undergoes formation reaction from RbCl and Rb₂CeCl₅ as the data showed a large C_p jump like Rb₃LaCl₆, but unlike Rb₃PrCl₆ and Rb₃NdCl₆.

Gromov et al. (1974) [42] did not report any phase change in the $X(\text{CeCl}_3) = 0-0.25$ region at 651 K. R. Benz et al. (1961) [45] were able to determine double solid phase transition in the same composition with CsCl-PuCl₃ system and in the RbCl-PuCl₃ system. Yin Sumin [47] reportedly detected phase decomposition of Rb₂CeCl₅ from $X(\text{CeCl}_3) = 0.33 - 1$ at 557 K which is inconsistent with the results given in Gromov's [42], Seifert's [48] and this work.

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Differential-scanning calorimetry confirmed a phase transition at 644 K within the range $0 < X(\text{CeCl}_3) < 0.33$. Gromov (1987) was unable to detect phase equilibria in this range, yet Seifert et al. (1986) [43] first investigation measured DTA signals at 651 K, and with X-ray pattern analysis suggesting Rb_3CeCl_6 was not stable at low temperature, and the DTA signal was assigned to the formation reaction of Rb_3CeCl_6 from RbCl and Rb_2CeCl_5 . L. Rycerz et al. (1999) [46] later measured the C_p of Rb_3CeCl_6 and measured an endothermic thermal effect of 8.5 kJ mol^{-1} at 651 K, assigning it to formation reaction based off Seifert's (1986) [48] earlier work by DTA. In a later report, by the same author; L. Rycerz (2004) [49], concluded that the small low-temperature effect measured at 411 K in Rb_3CeCl_6 was an order-disorder transition, while the higher-temperature thermal effect at 651 K represented a low temperature monoclinic Cs_3BiCl_6 -type phase transition to a high temperature cubic elpasolite-type structure.

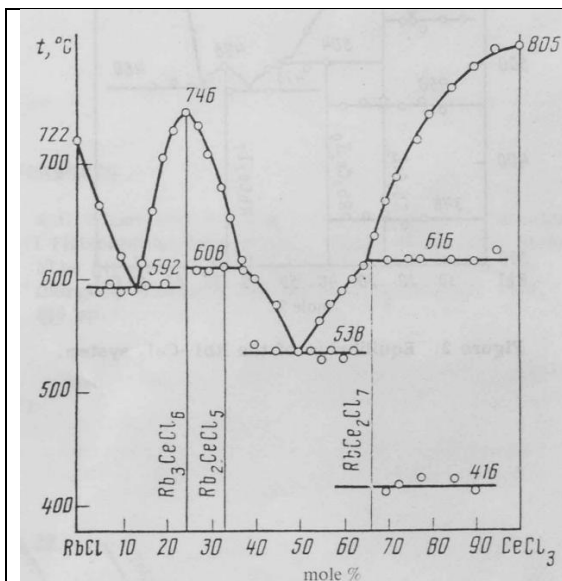


Fig 2. 1: RbCl-CeCl₃ phase diagram by Gromov et al. (1987) (with permission from Elsevier).

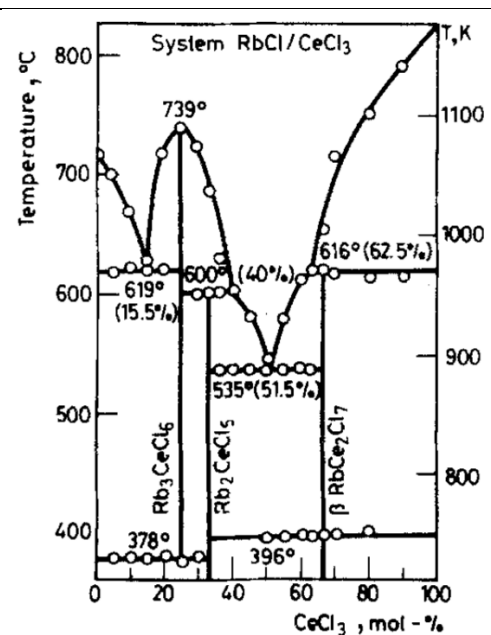


Fig 2. 2: RbCl-CeCl₃ phase diagram by Siefert et al. (1986) (with permission from Elsevier).

2.3.2 Crystallographic data

The crystallographic data of compounds are essential for understanding their structural and physical properties. These data provide insights into the atomic arrangement, space groups, and lattice parameters, which are essential for phase diagram assessments. In this study, two end member compounds; RbCl and CeCl₃ and three intermediate compounds; Rb₃MCl₆, Rb₂MCl₅ and RbM₂Cl₇ are reported in the literature. No crystallographic data exists for RbCl-PuCl₃ intermediate compounds, but due to the analogous nature of both systems in this work and for the two allotropes of Rb₃PuCl₆ and RbPu₂Cl₇ identified by microscopic examinations using a polarising microscope by Benz et al (1961) [45], it can be hypothesised that they will share identical space groups which can be confirmed by future work and XRD analysis.

Table 2. 1: Crystallography data of the end members of the RbCl-CeCl₃ system and their intermediate compounds

Chloride	<i>M</i> g mol ⁻¹	Space group	ρ g cm ⁻³	Ref
RbCl	120.921	<i>Fm</i> $\bar{3}$ <i>m</i> *	3.05	[50]
Rb ₃ CeCl ₆ (α)	609.237	<i>Fm</i> 3 <i>m</i>	2.99	[51]
Rb ₃ CeCl ₆ (β)	609.237	<i>n/a</i>	<i>n/a</i>	
Rb ₂ CeCl ₅	488.317	<i>oP</i> 32	3.36	[52]
RbCe ₂ Cl ₇ (α)	613.871	<i>n/a</i>	<i>n/a</i>	-
RbCe ₂ Cl ₇ (β)	613.871	<i>n/a</i>	<i>n/a</i>	-
CeCl ₃	246.475	<i>hP</i> 8	3.95	[53]
PuCl ₃	350.359	<i>hP</i> 8	5.79	[54]

2.3.3 Enthalpy of mixing

Enthalpy of mixing data exists for the for the ACl₃-CeCl₃ systems where A = Li, Na, K, Rb and Cs reported by Papatheodorou et al. (1974), and for many other alkali metal halides – lanthanide trichloride mixtures, as shown in **Fig. 2.11**. For RbCl-CeCl₃, experimental enthalpic data was used directly in the manual iterative process of

optimising the liquid solution. No experimental ΔH^M data exists for the of RbCl-PuCl₃ system. In this work, it was calculated using the linear prediction method as a function of ionic radii parameters proposed by Robelin et al. (2011) [55]. Other authors have used this method for RbCl-PuCl₃ in different thermochemical software [56], [57] and not including the four and six-coordinated complexes within the melt.

As later discussed in **Section 2.6.4**, the work of Schorne-Pinto et al. (2022) [58] focused on compiling all available experimental ΔH^M data and applying regression models to generate predictive fits for other binary chloride salt systems where experimental data are currently unavailable. However, while highly useful, their study did not address the shape of the ΔH^M curves obtained from raw experimental data for each binary system.

In contrast, the results reported by Papatherodorou et al. (1974) [40] show that the curve generated from the experimental data exhibits a broad minimum, which may indicate the presence of stable complex species at two or more compositions within the melt, rather than a single distinct minimum. This interpretation is further supported by the non-linear behaviour observed when the data are expressed in terms of the enthalpic interaction parameter λ^M). In this work, linear regression was applied to previously available experimental data, similar to the approach of Schorne-Pinto et al. [58], but with additional emphasis on preserving the curve shape observed by Papatherodorou et al. [40], to ensure a more reliable representation of the liquid solution model.

Shown in **Fig. 2.11**, the calculated RbCl-CeCl₃ data, were plotted as function of ionic radii δ_{12} parameter. The δ_{12} parameter is defined as:

$$\delta_{12} = \frac{[r_A^+ + r_{Cl}^-] - [r_M^{3+} + r_{Cl}^-]}{[r_A^+ + r_{Cl}^-][r_M^{3+} + r_{Cl}^-]} \quad (2.1)$$

Where r_A^+ is the ionic radius of the alkali cation in the systems, r_M^{3+} is the ionic radii of the trivalent metal cation and r_{Cl}^- is the ionic radii of chloride in each binary system. An assessment of existing ΔH^M datasets as a function of δ_{12} (highlighted later in **Fig. 2.11**) confirmed the presence of a comparable trend. One trend common to all mixtures, including AlkX-MX₃, where Alk = Li, Na, K, Rb, Cs and X = F,

Cl, Br, I binary systems, that with heavier Alk cation for common anion systems, i.e. $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ and $X = \text{F}$, the minimum ΔH^M becomes more negative. Another trend observed in AlkX-MX_3 binary mixtures is that the minimum ΔH^M occurs near $X(\text{MX}_3) = 0.5$ for LiX-based systems but shifts toward $X(\text{MX}_3) = 0.3\text{--}0.4$ as the alkali metal becomes heavier. This shift indicates stronger complexation and Short-Range Ordering (SRO) in the alkali halide-rich compositions.

2.4 Thermodynamic modelling of the liquid solution

Computational models are required to calculate the chemical equilibrium, reaction kinetics, transport properties and thermochemical behaviour of complex multicomponent multiphase systems. This becomes more complicated as the multicomponent and multiphase systems change with composition over time – which will occur in an MSFR as the fission reaction progresses, and fission products accumulate and higher actinides form from neutron capture. Experimental data are required as input for the model parameters, yet most data do not exist, or experiments are too complex to be carried out for extraction of said parameters. Therefore, to enable predictions in more complex multicomponent multiphase systems, robust thermodynamic descriptions of simpler systems, e.g. at Beginning of Life (BOL), are essential. The computational models are based on Gibbs free energy minimisation can be calculated using modern software, in this case, *Factsage Version 8.3*. For multi-component systems, thermodynamic data is firstly taken from pure end-member components, relevant experimental data and the interaction parameters.

Solution phases' thermodynamic properties must be established as a function of composition, temperature and pressure to calculate phase equilibria and other possible chemical reaction pathways that involve the molten salt solution. For this reason, many thermodynamic models have been developed to describe various organic and inorganic solutions for solid, liquid and gas phases. It is important to note that the gas phases are completely miscible, but solid and liquid phases can exhibit common phase separation, i.e. immiscibility. Non-ideal gas behaviour can

be modelled in various ways; however, in this work, under the high temperatures (>673 K) and ambient pressures typical of an operational MSFR, gas models are not accounted for yet. These effects should be evaluated and incorporated in future studies if the liquid solution properties prove promising for a MSFR fuel and design. Generally applicable to all solution phases, the Gibbs energy, G is given by the formula:

$$G = G^\circ + \Delta G_{mix}^{ideal} + \Delta G_{mix}^{excess} \quad (2.2)$$

Where G° is the standard Gibbs energy of the pure components within the solution phase of interest, ΔG_{mix}^{ideal} is the ideal Gibbs energy of mixing and ΔG_{mix}^{excess} is the excess Gibbs energy of mixing that introduces the non-ideal contributions into the MS solution.

Gibbs energy minimisations are performed computationally for complex systems and can determine true chemical equilibrium once the data from all phases are input into the model. The Gibbs energy is hence described as:

$$G = \sum_i n_i \bar{G}_i \quad (2.3)$$

Where n_i is the number of moles of component i , and $\bar{G}_i$ is the calculated or known chemical potential of component i , for a given set of fixed constraints, such as P , T and overall composition. In **Section 2.4**, the framework of the most relevant thermodynamic model used to best describe molten salt solutions that exhibit SRO is further explained. The C_p can be derived mathematically by a second order partial derivative of the Gibbs energy function and further validated by experimental measurement.

The modified quasi-chemical model quadruplet approximation (MQMQA), proposed by Pelton et al. (2001) [28] was used to model the excess Gibbs energy of the liquid phase. The quadruplet model consists of two sub-lattices, one consisting of cations A and B (representing M³⁺ and Rb⁺) and anion Cl⁻ (in this work only chloride anion is present). The quadruplet is the fundamental unit in this model. In previous models, i.e. QCM pair approximation, the first-nearest neighbours (FNN)

interactions rather than the second-nearest neighbours (SNN) were modelled to be the dominant influence on the excess terms, shown in **Fig. 2.3**. The quadruplet approximation is updated and treats FNN and SNN interactions simultaneously for determining optimised excess parameters of the liquid solution.

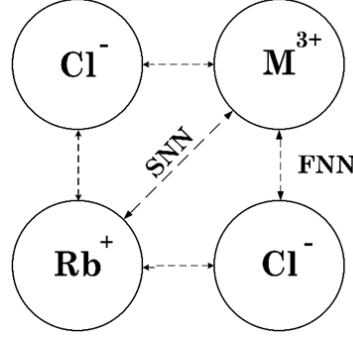
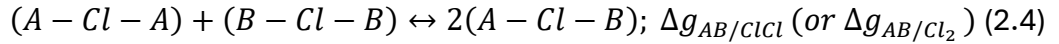
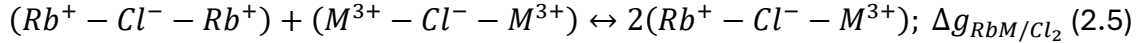


Fig. 2. 3: Schematic of one quadruplet model illustrating first-nearest neighbour (FNN) and the second-nearest neighbour (SNN) with two cations (Rb⁺) and (M³⁺, where M = Ce, Pu) and two anions both (Cl⁻) in this case.

The transfer reaction between FNN and SNN pairs are expressed as:



or



$\Delta g_{RbM/Cl_2}$ is an empirical parameter and may be composition dependant, if $\Delta g_{RbM/Cl_2} = 0$ then random mixing occurs, if $\Delta g_{RbM/Cl_2} < 0$, then Equation 2.4 is displaced to the right with (Rb⁺-Cl⁻-M³⁺) pairs becoming predominant.

The Gibbs energy change $\Delta g_{AB/Cl_2}$ associated with the SNN-FNN reaction is given by:

$$\Delta g_{RbM/Cl_2} = \Delta g_{RbM/Cl_2}^0 + \sum_{i \geq 1} g_{RbM/Cl_2}^{i0} x_{RbM/Cl_2}^i + \sum_{j \geq 1} g_{RbM/Cl_2}^{j0} x_{RbM/Cl_2}^j \quad (2.6)$$

Where $\Delta g_{RbM/Cl_2}^0$, g_{RbM/Cl_2}^{i0} and g_{RbM/Cl_2}^{j0} are composition independent coefficients that may vary with temperature. Note that the terms with subscript RbM/Cl_2 and MRb/Cl_2 represent the same pairs and can be used interchangeably. x_{RbM/Cl_2}^{ij} is composition dependant function, defined as the fraction to cation-cation pair mole fractions X_{RbRb/Cl_2} , X_{RbM/Cl_2} and $X_{M^{3+}M^{3+}/Cl_2}$:

$$X_{RbM/Cl_2}^{Rb} = \frac{X_{RbRb/Cl_2}}{X_{RbRb/Cl_2} + X_{RbM/Cl_2} + X_{MM/Cl_2}} \quad (2.7)$$

As the composition of RbCl-MCl₃ binary systems changes, the quadruplet approximation model must maintain other parameters to satisfy the conservation of charge whilst simultaneously considering how the FNN and SNN coordination number varies. By assuming the cation SNN coordination number and the charges of cation/anion remains constant, the anion SNN coordination numbers are fixed in the quadruplet by:

$$\frac{q_{Rb}}{Z_{RbM/Cl_2}^{Rb}} + \frac{q_M}{Z_{RbM/Cl_2}^M} = \frac{q_{Cl}}{Z_{RbM/Cl_2}^{Cl}} + \frac{q_{Cl}}{Z_{RbM/Cl_2}^{Cl}} \quad (2.8)$$

Where q_i are the charges of anions and cations, and Z_{RbM/Cl_2}^i are the SNN coordination number of the respective ion in each quadruplet. For each end-member, the quadruplet formations include (M³⁺-Cl-M³⁺), (Rb⁺-Cl-Rb⁺), (Rb⁺-Cl-M³⁺) SNNs. Their excess Gibbs energy expressions are expressed as $\Delta g_{RbRb/Cl_2}$, $\Delta g_{RbM/Cl_2}$ and $\Delta g_{MM/Cl_2}$.

The current work introduces a mixture of M_{iv}^{3+} and M_{vi}^{3+} (with coordination numbers in indices) into the pure liquid MCl₃ as the same complexes and surrogate complexes were identified in Raman spectroscopy studies with MCl₃ and AlkCl mixtures (Alk = Li, Na, K; M = Ce, La) [39], [40]. X. Song et al. (2023) [59], in a comprehensive review comparing techniques for assessing the structural and coordination states of molten ions, report that Raman spectroscopy requires no sample pretreatment, offers straightforward setup, rapid measurement, and high sensitivity; however, its principal limitation is that the structural information obtained is predominantly qualitative. The review further highlights that variations in molten salt systems, contingent on the constituent end members, can give rise to markedly different liquid complexes; for example, the formation of BeF₂²⁻, Be₂F₇³⁻ and Be₃F₁₀⁴⁻ in the LiF-BeF₂ binary system. This permits two different compositions of Second Nearest Neighbour-Short Range Ordering (SNN-SRO). M_{iv}^{3+} is the four-coordinated M³⁺, corresponding to the [MCl₄]⁻ “complex-anion”, and M_{vi}^{4+} is the six-coordinated M³⁺, corresponding to the [MCl₆]³⁻ “complex-anion”.

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Following this methodology, the following complexes [MCl₄]⁻ and [MCl₆]³⁻ have SRO at compositions $X(\text{MCl}_3)$ at 0.25 and 0.5 respectively. The results show that this model can satisfactorily reproduce the newly measured experimental phase diagram data in this work whilst maintaining the calculated enthalpy of mixing.

As this model incorporates various uranium cations, pure CeCl₃ and PuCl₃ liquid becomes a mixture of M_{iv}^{3+} and M_{vi}^{3+} cation species and respectively F⁻ anions. From the Raman spectroscopy data produced by Papatheodorou et al. (1974) [40] with increasing MCl₃, M_{vi}^{3+} is the dominant species. Further justification of the dominant species having maximum SRO at the composition of 50 mol% in the RbCl binary salt mixtures, seen by general deep eutectic at 0.50 $X(\text{MCl}_3)$. Therefore, to have small amounts of M_{iv}^{3+} in this range, the liquid end-members $M_{iv}\text{Cl}_4$ and $M_{vi}\text{Cl}_4$ have been destabilised by adding a positive Gibbs energy contribution as shown in **Table 2.6**. The small contribution to the entropy of configuration due to the mixing of the different cationic Ce or Pu species does not affect the melting points of MCl₃.

The Factsage software calculates the Gibbs free energy of the liquid solution by the by summing the Gibbs free energies of the various quadruplets along with the energy contributed by the configurational entropy resulting from the distribution of the quadruplets on the lattice sites as expressed below:

$$G = \sum_{i=U_{iv}U_{vi}} \sum_{j=Rb} \sum_{k=Cl} n_{ij/kk} g_{ij/k}^0 - T\Delta S^{config} \quad (2.9)$$

Where $n_{ij/kk}$ is the number of moles of the ij/kk quadruplet, $g_{ij/k}^0$ is the molar Gibbs free energy of the ij/k quadruplet, and ΔS^{config} is the configurational entropy of mixing. A definitive mathematical description of the entropy term is not presently established; however, an appropriate expression was proposed by Pelton et al. (2000) [60]. $n_{ij/kk}$ is the number of moles of quadruplets, which requires a minimisation of the Gibbs free energy of the molten salt binary solution at a known temperature, pressure and composition – this embodies the equilibrium configuration of both the FNN and SNN. Although the SNN numbers are not used to physically characterise the complexes within the salt solution, they are model parameters allowing them to define the composition of which maximum SRO

occurs. This is constrained by charge neutrality, by Equation 2.9 and following Z numbers used in this model in **Table 2.2**.

Table 2. 2: SNN “coordination numbers” for quadruplets ABXX (with X = Cl) used in the MQMQA for the liquid to model SRO at compositions X(MCl₄) at 0.25 and 0.50 for [MCl₆]³⁻ and [MCl₄]⁻ respectively.

A	B	Y	$Z_{AB/YY}^A$	$Z_{AB/YY}^B$	$Z_{AB/YY}^Y$	$Z_{AB/YY}^Y$
Rb	Ce _{iv}	Cl	6	6	3	3
Rb	Ce _{vi}	Cl	2.4	7.2	2.4	2.4
Rb	Pu _{iv}	Cl	6	6	3	3
Rb	Pu _{vi}	Cl	2.4	7.2	2.4	2.4

The modified solution model builds on the composition dependent Gibbs energy exchange Eq. 14 as there are more than two simple cations; Rb⁺ and M³⁺, there are the proposed three; Rb⁺, M_{iv}³⁺ and M_{vi}³⁺. Mole fraction pairs given in Equation 2.10 are now used as composition variables $\chi_{AB/YY}$ or χ_{AB/Y_2} , accordingly proposed as the following:

$$\chi_{RbM_{iv}/Cl_2} = \chi_{RbM_{vi}/Cl_2} = X_{Rb_2/Cl_2} \quad (2.10)$$

$$\chi_{M_{iv}Rb/Cl_2} = \chi_{M_{vi}Rb/Cl_2} = X_{(M_{iv})_2/Cl_2} + X_{(M_{vi})_2/Cl_2} + X_{U_{iv}U_{vi}/Cl_2} \quad (2.11)$$

$$\chi_{M_{iv}M_{vi}/Cl_2} = \frac{(X_{M_{iv}M_{vi}/Cl_2})}{(X_{(M_{iv})_2/Cl_2} + X_{(M_{vi})_2/Cl_2} + X_{M_{iv}M_{vi}/Cl_2})} \quad (2.12)$$

$$\chi_{M_{vi}M_{vi}/Cl_2} = \frac{(X_{M_{vi}M_{vi}/Cl_2})}{(X_{(M_{iv})_2/Cl_2} + X_{(M_{vi})_2/Cl_2} + X_{M_{iv}M_{vi}/Cl_2})} \quad (2.13)$$

As Equation 2.8 represents the total Gibbs free energy on the overall system as a given composition and temperature, the expression for the configurational entropy

of mixing (ΔS^{conf}) necessitates FNN pair fractions to mitigate convergence between quadruplets and other sets of quadruplets. The parameter ζ is introduced which is defined as the number of quadruplets emanating from a FNN pair, in this case, a Rb^+-Cl^- or $\text{M}^{3+}-\text{Cl}^-$ pair. In other molten salt models using the improved MQMQA, authors have varied ζ , normally to account for the reciprocal systems containing significant differences of anionic radii, such as F^- and CO_3^{2-} . In this work, ζ has been kept equal to 2.4, as proposed by Chartrand et al. [61] for Li^+ , Na^+ , K^+ , Mg^{2+} , $\text{Ca}^{2+}/\text{F}^-$, Cl^- reciprocal system.

Lastly, the $\Delta g_{\text{RbM}/\text{Cl}_2}$ of all the quadruplets were manually optimised without the use of Optisage software to fit the previous and new experimental phase diagram data explored in this work – alongside the anticipated enthalpy of mixing. The coefficients are usually expressed as $A + BT$, where A and B are optimised individually to achieve the possible fit to the data. In this work, as the $\text{RbCl}-\text{MCl}_3$ binary system is more complex, exhibiting two different eutectics, rather than a simple singular eutectic found in the $\text{NaCl}-\text{RbCl}$ system, more coefficients were introduced to account for the larger non-ideal properties, A - typically being the constant enthalpic term, and the latter terms being entropic that vary with temperature, such as:

$$\Delta g_{\text{RbU}/\text{Cl}_2} = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E \cdot T^3 \quad (2.14)$$

2.5 Experimental method

2.5.1 Reagent preparation and handling

All salt samples were stored in a glovebox under dry nitrogen atmosphere $>1\text{ppm}$ H_2O , $>5\text{ppm}$ O_2 . Anhydrous CeCl_3 (99.99% pure) and RbCl (99.8% pure) were purchased from Sigma Aldrich. The CeCl_3 arrived in a sealed glass ampoule and was tested for purity by DSC measurement – one clear and sharp peak was observed and melting point of 1081 K and enthalpy of fusion of 55.3 kJ mol^{-1} which was in line with literature. The RbCl , (99.8% pure) results indicated the correct melting point of 991 K and enthalpy of fusion of 24.3 kJ mol^{-1} in line with the literature.

Due to the maximum sample weight for TGA/DSC analysis being approximately 15 mg, and the highest-precision balances available having a sensitivity of ± 0.1 mg, mass measurements were subject to a relatively large margin of error. This uncertainty varied between experiments, depending on the weighing method employed. Although a ± 0.1 mg balance was available inside the glovebox, its accuracy was significantly affected by fluctuations in internal pressure and gas flow, even when the balance's glass doors were closed. Attempts to mitigate this, including disabling internal blowers and conducting measurements at constant pressure did not resolve the issue. To improve accuracy, crucibles were sealed in gas-tight glass vials and transported to an equivalent ± 0.1 mg balance outside the glovebox. This approach yielded more consistent mass readings; however, day-to-day variability persisted. This was traced to changes in ambient humidity, which influenced the balance due to electrostatic effects associated with the insulating glass vial. The problem was resolved by incorporating a conductive aluminium strip into the vial design, ensuring electrical contact between the Ni-201 crucible and the balance's grounded base. While this effectively reduced electrostatic interference and improved measurement reliability, the overall process of transferring samples in and out of the glovebox remained time-consuming.

2.5.2 Crucible choice and design

No commercially available crucible exists suitable for molten salt tests at high temperatures, prior papers have been published highlighting how challenging custom designing crucibles are by Piro et al. (2021) [62] and Beneš (2010) [63]. A custom-made crucible was successfully developed at Lancaster University shown in **Figs. 2.4&2.5** showing phase transitions (**Fig. 2.7**) of the RbCl-CeCl₃ binary system in-line with data from [48]. The crucible was first developed and validated in this work and was subsequently employed in later molten salt experiments to identify additional phase equilibria, although these studies were published earlier by Findlay et al. (2026) [64], [65].

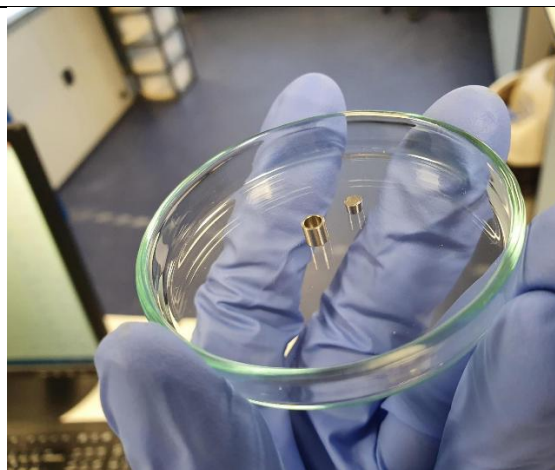


Fig. 2. 4: Ni-201 crucible with SUS316L lid in petri dish pre-sealing.

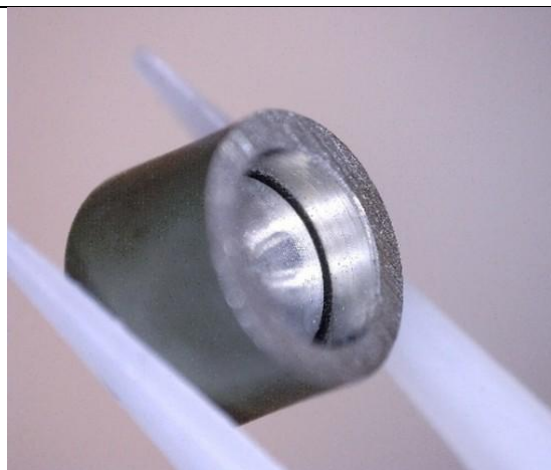


Fig. 2. 5: Crucible with bottom end sanded open for corrosion inspection post experiment (88.8 mol% RbCl - 11.2 mol% CeCl₃).

The TGA/DSC instrument used in this study was the STA7000 series from Hitachi, which imposes a strict maximum mass limit of 400 mg for both the sample and reference holders. Accounting for the use of 10 mg alumina disks placed beneath the crucibles to prevent metallic interactions with the holder, and 20 mg of salt sample, the crucibles themselves were required to weigh equal to or less than 370 mg. The finalised post-prototype design for the total mass of both the crucible and lid was 330 mg.

Previous studies on custom DSC crucible designs for molten salt applications consistently emphasize key features: good thermal contact with the holder, corrosion resistance, and hermetic sealing. Most designs utilise reusable stainless-steel crucibles with screw-type or welded lids and are internally lined with nickel to enhance corrosion resistance. However, such configurations could not be adopted here due to the mass constraint and the inability to perform welding operations within the glovebox.

One main challenge was the requirement to develop a suitable sealing mechanism, given the absence of facilities for performing in-situ welding inside the nitrogen-filled glovebox environment. While molten chloride salts typically exhibit low vapor pressures at elevated temperatures, the use of small sample sizes (e.g., ~20 mg)

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means that even minor vaporisation can result in measurable mass loss. This effect is further amplified by the flowing inert gas within the DSC furnace, which enhances volatilization through convective mass transfer. It was found that hermetically sealing the crucible was necessary to avoid composition shift as such small quantities of salt would have more effect due to this phenomenon.

To address the issues of corrosion and sealing, an interference-fit method was developed using a manually operated hydraulic press. Trials revealed that when both the crucible and lid were fabricated from the same alloy, galling-induced leakage occurred, resulting in a failed experiment. The combination of a Ni-201 crucible and SUS316L lid effectively eliminated galling during the sealing process and enabled a fully hermetic seal; however, this configuration rendered the crucibles single-use. Despite the increased resource consumption, this approach substantially improved radiological safety for both laboratory personnel and the DSC equipment.

The bases of some crucibles were sanded open to inspect for signs of corrosion. It was found that with visual inspection alone corrosion was not noticeably seen in

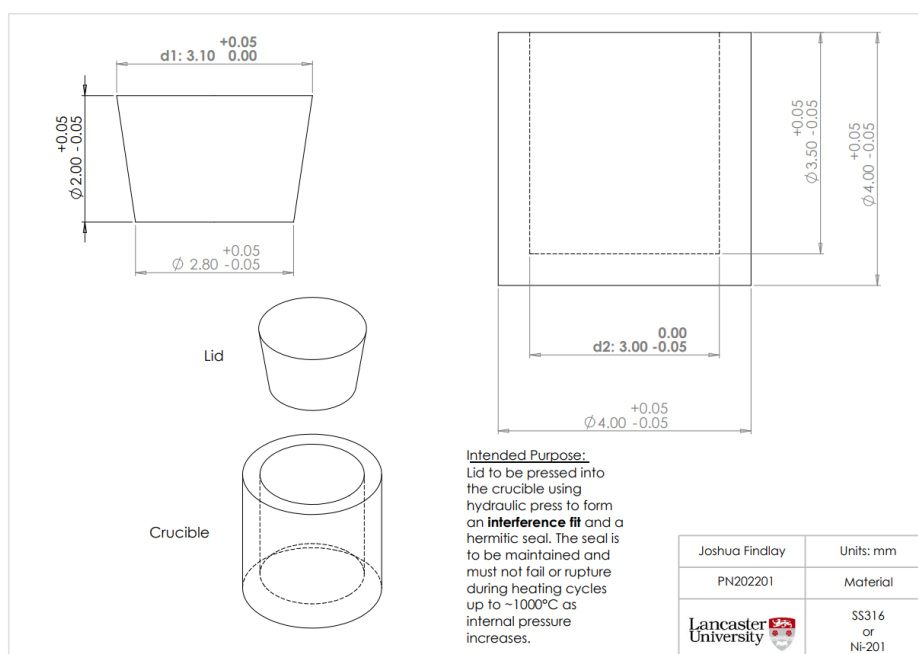


Fig 2. 6: Engineering design drawing of the Ni-201 crucible and SUS316L lid, specifying machining tolerances and optimised for cost-efficient bulk CNC manufacturing, achieving a unit cost of \$3.26 USD per crucible.

Custom developed DSC crucibles described in this work by Benes [66], substantially larger (~200g) than the crucibles in this work (0.37g), were engineered for molten salt analysis and re-use, however, authors did not specify how often the inner nickel liner was replaced or extent of corrosion observed. Although low-mass, single-use crucibles were not the primary design objective, since reusable crucibles are often considered more economical, the lighter disposable crucibles offered the added benefits of significantly improved sensitivity, due to reduced steel mass, minimised corrosion and low-cost (shown in **Fig. 2.6**). Prior studies rarely address crucible reusability, although solidified salt is typically difficult to remove without aqueous dissolution, thereby preventing reuse of the salt for subsequent experiments.

2.5.3 TGA/DSC experimental procedure

Once the Ni-201 crucible had been sealed with the SUS316L lid, it was transferred directly to the TGA/DSC (Hitachi STA7200) sample holder. Once loaded, the TGA/DSC furnace chamber was closed and initially purged with argon gas for 1 hour before each experiment. The steady flowrate of argon aided in prevention of oxidation of the exterior surfaces of the Ni-201 and SUS316L, thus ensuring structural integrity.

The experiment involved four heating cycles conducted at rates of 10 K·min⁻¹, 8 K·min⁻¹, 5 K·min⁻¹ and 5 K·min⁻¹, with the first heating cycle disregarded. This was followed by three cooling cycles at the same rates: 10 K·min⁻¹, 8 K·min⁻¹, and 5 K·min⁻¹.

For operator safety, the furnace remained locked throughout all thermal cycles and until it cooled back to room temperature. Additionally, the use of a hermetically sealed crucible helped prevent the release of corrosive chloride salt vapours, protecting the furnace's internal components.

At the conclusion of the experiment, two datasets were collected: thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The

TGA monitors sample mass changes as a function of temperature using an internal balance, therefore provided if the crucible is unsealed, mass change can indicate phase changes through volatilisation or sublimation, decomposition, or other thermal events.

Meanwhile, the DSC measures the difference in heat flow between the sample crucible and an empty reference crucible. Phase changes or chemical reactions in the sample cause heat absorption (endothermic) or release (exothermic), resulting in distinct peaks on the DSC curve.

The STA7200 thermometer's precision is ± 0.001 K - therefore, the primary source of error in the TGA measurements stems from manual calibration, which involves recording standard transitions and extrapolating transition temperatures (T^r). Following the equipment's manual, two compounds of high purity (99.99%) were used for the temperature calibration. One sample with low temperature transition, KNO₃ at 401.7 K and one with a high temperature transition, Ag at 1234.8 K to ensure that all sample measurements fell within the calibrated temperature range. According to the Netzsch manual [67], calorimetric measurements employed calibrants exhibiting solid-solid and solid-liquid phase transitions over a wide temperature range, in place of standard metals (with the exception of Ag), which risk alloying with the Ni-201 crucible or SUS316L lid. The calibrants used were KNO₃, KClO₄, CsCl, BaCO₃, and Ag.

2.6 Results

2.6.1 Thermodynamic data and crystal structures for pure compounds

The Gibbs energy function of a pure compound is given by:

$$G(T) = \Delta_f H^\circ(298) - S^\circ(298)T + \int_{298}^T C_p(T) dT - T \int_{298}^T \frac{C_p(T)}{T} dT \quad (2.15)$$

where $\Delta_f H^\circ$ is the standard enthalpy of formation, S° is the standard absolute entropy, both evaluated at a reference temperature (298K) and C_p is the isobaric molar heat capacity which is expressed as a polynomial as a function of temperature:

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$$C_p = a + bT + cT^2 + dT^{-2} + eT^3 \quad (2.16)$$

Where a, b, c and d are dimensionless constants and more terms can be added if necessary. For the purpose of this work, pure components of within this study are given in **Table 3** with their thermodynamic properties. The heat capacity (C_p) functions of intermediate solid compounds were determined using the Neumann-Kopp method within the FactSage Compounds module, implemented through the Mixer function.

Table 2. 3: Thermodynamic data of all pure components in RbCl-CeCl₃ and RbCl-PuCl₃ systems

Compound	T range (K)	$\Delta H_f^{\circ}{}_{298.15K}$ (J·mol ⁻¹)	$S^{\circ}{}_{298.15K}$ (J·K ⁻¹ ·mol ⁻¹)	$C_{p,m} = a + b \cdot T + c \cdot T^2 + d \cdot T^{-2}$				Ref
				a	b	c	d	
RbCl (s)	298.15 – 1500	435220.0	95.23	48.51268	0.01256576	95.11015	-3.80492E-9	[44]
	1500 - 2400			25.05421037	0.037889418	5533098.364	-7.55943E-6	
	2400 - 3400			73.4				
RbCl (l)	298.15 - 3400	-422526.77	98.44	73.4				[44]
CeCl ₃ (s)	298.15 – 1400	-1059700	151.42	90.9772	0.0358123	-271530		[44]
	1400 - 2300			23.8740662	0.109906341	14156259.31	-2.23758E-5	
	2300 – 3400			161.05				
CeCl ₃ (l)	298.15 - 3000	-1042566.19	136.70	161.05				[44]
Rb ₂ CeCl ₆ (α)	298.15 – 1400	-2397771.156	468.86	236.51524	0.07350958	-271244.66955	-1.141476E-8	This work
	1400 - 1500			169.41210622	0.147603621	14156544.64045	-2.238721476E-5	
	1500 - 2300			99.03669733	0.223574595	30755554.402	-4.505409E-5	
	2300 - 2400			236.21263111	0.113668254	16599295.092	-2.267829E-5	
	2400 - 3000			381.25				
Rb ₂ CeCl ₆ (β)	298.15 – 1400	-2389251.406	482.11	236.51524	0.07350958	-271244.66955	-1.141476E-8	This work
	1400 - 1500			169.41210622	0.147603621	14156544.64045	-2.238721476E-5	
	1500 - 2300			99.03669733	0.223574595	30755554.402	-4.505409E-5	
	2300 - 2400			236.21263111	0.113668254	16599295.092	-2.267829E-5	
	2400 - 3000			381.25				
Rb ₂ CeCl ₆	298.15 – 1400	-1951115.367	371.88	188.00256	0.06094382	-271339.7797	-7.60984E-9	This work
	1400 - 1500			120.89942622	0.135037861	14156449.5303	-2.238340984E-5	
	1500 - 2300			73.98248696	0.185685177	25222456.038	-3.749466E-5	
	2300 - 2400			211.15842074	0.075778836	11066196.728	-1.511886E-5	
	2400 - 3000			307.85				

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RbCe ₂ Cl ₇ (α)	298.15 – 1400	-2565230.59	426.07	230.46708	0.08419036	-542964.88985	-3.80492E-9	This work
	1400 - 1500			96.26081244	0.232378442	28312613.73015	-4.475540492E-5	
	1500 - 2300			72.80234281	0.2577021	33845616.984	-5.231103E-5	
	2300 - 2400			347.15421037	0.037889418	5533098. 364	-7.55943E-6	
	2400 - 3000			395.5				
RbCe ₂ Cl ₇ (β)	298.15 – 1400	-2563874.59	428.07	230.46708	0.08419036	-542964.88985	-3.80492E-9	This work
	1400 - 1500			96.26081244	0.232378442	28312613.73015	-4.475540492E-5	
	1500 - 2300			72.80234281	0.2577021	33845616.984	-5.231103E-5	
	2300 - 2400			347.15421037	0.037889418	553 3098.364	-7.55943E-6	
	2400 - 3000			395.5				
PuCl ₃ (s)	298.15 – 1040	-959600.00	161.70	91.35	0.024	240000		[68]
	1040 – 1450			144.1391155	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			122.15252				
PuCl ₃ (l)	298.15 - 1040	-904600.01	214.53	91.35	0.024	240000		[68]
	1040 - 1500			145				
Rb ₃ PuCl ₆ (α)	298.15 - 950	-2276435.75	500.00	236.88804	0.06169728	240285.33045	-1.141476E-8	This work
	950 – 1040			192.8153391	0.150270903	2214743.742	-4.68567E-5	
	1040 – 1328			245.6044546	0.121016221	-19722461.068	-4.87948E-5	
	1328 – 1450			331.77606064	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			309.78946514				
Rb ₃ PuCl ₆ (β)	298.15 - 950	-2258314.70	527.00	236.88804	0.06169728	240285.33045	-1.141476E-8	This work
	950 – 1040			192.8153391	0.150270903	2214743.742	-4.68567E-5	
	1040 – 1328			245.6044546	0.121016221	-19722461.068	-4.87948E-5	
	1328 – 1450			331.77606064	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			309.78946514				
Rb ₂ PuCl ₅	298.15 - 950	-1845919.429	386.80	188.37536	0.04913152	240190.2203	-7.60984E-9	This work
	950 – 1040			158.9935594	0.108180602	1556495.828	-3.12378E-5	
	1040 – 1328			211.7826749	0.07892592	-20380708.982	-3.31759E-5	
	1328 – 1450			269.23041226	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			247.24381676				
RbPu ₂ Cl ₇ (α)	298.15 - 950	-2358182.464	451.63	231.21268	0.06056576	480095.11015	-3.80492E-9	This work
	950 – 1040			216.5217797	0.090090301	1138247.914	-1.56189E-5	
	1040 – 1328			322.1000107	0.031580937	-42736161.706	-1.94951E-5	
	1328 – 1450			350.82387938	-0.010509364	-43394409.62	-3.8762E-6	
	1450 - 2000			306.85068838				
RbPu ₂ Cl ₇ (β)	298.15 - 950	-23504416.664	463.63	231.21268	0.06056576	480095.11015	-3.80492E-9	This work
	950 – 1040			216.5217797	0.090090301	1138247.914	-1.56189E-5	

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1040 – 1328		322.1000107	0.031580937	-42736161.706	-1.94951E-5
1328 – 1450		350.82387938	-0.010509364	-43394409.62	-3.8762E-6
1450 - 2000		306.85068838			

2.6.2 Phase equilibria measurements of the RbCl-CeCl₃ system

As demonstrated by **Fig. 2.7**, the custom crucible designed with minimal mass resulted in much excellent sensitivity that could detect smaller phase transitions by the STA7200 thermocouples. The DSC cooling curves were not used as transition temperatures as they were highly inconsistent with cooling rates. This phenomenon is common with halide salt mixtures due to supercooling, though, they did produce very clear and sharp peaks, which was useful for identifying the number of phase transitions at each composition tested. The heating cycle data were used for phase equilibria points in this study, as it was noted the interpolated phase transition temperatures were not heating rate dependant and produced highly consistent results.

DSC measurements by Rycerz et al. (1999) [46] of the Rb₃CeCl₆ polymorphic phase transition were measured to be 8.5 kJ mol⁻¹ endothermic enthalpy change. This phase transition was consistent with measurements in this study and was incorporated into the model optimised in this work. Integrating the polymorphic transition into the model of the Rb₃CeCl₆ also aligns with the Rb₃PuCl₆ compound and its two allotropes. Similarly, the s₁ → s₂ (α → β) transition of RbCe₂Cl₇ was measured through DSC in this work to be endothermic of 1.3 kJ mol⁻¹ and was integrated into this model. Initial iterations of the CALPHAD optimisation incorporated comparable enthalpy values for the phase transitions of the surrogate compounds Rb₃PuCl₆ and RbPu₂Cl₇. However, it was later determined that reproducing the phase diagram accurately and maintaining the stability of the s1(α) plutonium-based phases at lower temperatures required the use of slightly larger endothermic ΔH^{tr} values of 18.1 kJ mol⁻¹ and 7.77 kJ mol⁻¹ respectively.

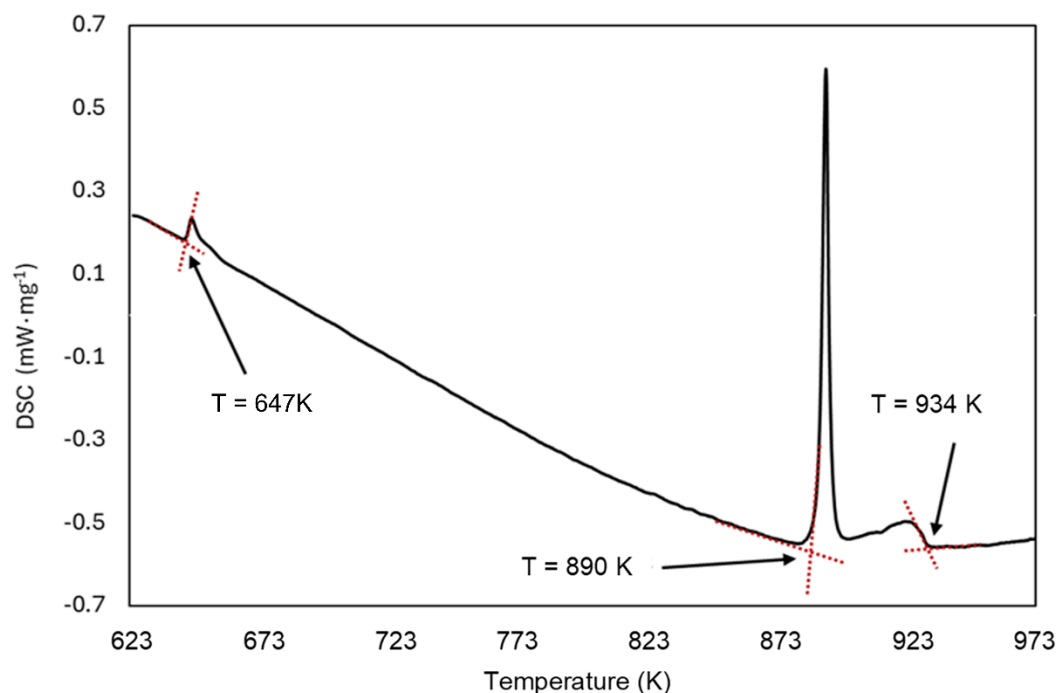


Fig. 2. 7: Raw DSC data RbCl-CeCl₃ (88.8 mol% – 11.2 mol%), heating rate as 5 K·min⁻¹ and extrapolated points used as thermal event data.

The invariant point data are reported in **Table 4** comparing literature data with data gained in this study from DSC signals.

Table 2. 4: Invariant point comparison of the DSC results with key experimental points of the RbCl-CeCl₃ system.

System	Reaction	Invariant Point		Ref.
		T (K)	X _{RbCl}	
RbCl-CeCl ₃	Liquid → RbCl + Rb ₂ CeCl ₆	889	0.15	[47]
		865	0.14	[42]
		892	0.10	[43]
		890	0.15	This work
	RbCl + Rb ₂ CeCl ₅ → Rb ₃ CeCl ₆	n/d	n/d	[47]
		n/d	n/d	[42]
		651	0.25	[43]
		644	0.25	This Work
	Liquid → Rb ₃ CeCl ₆ (s ₂)	1023	0.25	[47]
		1019	0.25	[42]

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		1017	0.25	[43]
		1013	0.25	This work
	$\text{Rb}_3\text{CeCl}_6 (s_2) \rightarrow \text{Rb}_3\text{CeCl}_6 (s_1)$	n/d	n/d	[47]
		n/d	n/d	[42]
		651	0.25	[43]
		644	0.25	This work
	$\text{Liquid}' + \text{Rb}_3\text{CeCl}_6 (s_2) \rightarrow \text{Rb}_2\text{CeCl}_5$	873	0.33	[47]
		882	0.33	[42]
		873	0.33	[43]
		870	0.33	This work
	$\text{Liquid} \rightarrow \text{Rb}_2\text{CeCl}_5 + \text{RbCe}_2\text{Cl}_7 (s_2)$	806	0.50	[47]
		811	0.50	[42]
		808	0.50	[43]
		807	0.50	This work
	$\text{Liquid}' + \text{CeCl}_3 \rightarrow \text{RbCe}_2\text{Cl}_7(s_2)$	886	0.66	[47]
		889	0.66	[42]
		889	0.66	[43]
		887	0.66	This work
	$\text{RbCe}_2\text{Cl}_7 (s_1) \rightarrow \text{RbCe}_2\text{Cl}_7(s_2)$	n/d	n/d	[47]
		689	0.66	[42]
		669	0.66	[43]
		677	0.66	This work

Table 2. 5: Invariant point comparison of the DSC results with key experimental points of the RbCl-PuCl₃ system from R. Benz with and the calculated phase diagram presented in this work.

System	Reaction	Invariant Point		Ref.
		T (K)	X _{RbCl}	
RbCl-PuCl ₃	$\text{Liquid} \rightarrow \text{RbCl} + \text{Rb}_2\text{PuCl}_6$	903	0.14	[45]
		901	0.14	This work

	$\text{Rb}_3\text{PuCl}_6 (s_1) \rightarrow \text{Rb}_3\text{PuCl}_6 (s_2)$	671	0.33	[45]
		671	0.33	This work
	Liquid $\rightarrow \text{Rb}_3\text{PuCl}_6 (s_2)$	1047	0.25	[45]
		1046	0.25	This work
	Liquid' + $\text{Rb}_3\text{PuCl}_6 (s_2) \rightarrow \text{Rb}_2\text{PuCl}_5$	833	0.33	[45]
		834	0.33	This work
	Liquid $\rightarrow \text{Rb}_2\text{PuCl}_5 + \text{RbPu}_2\text{Cl}_7 (s_2)$	777	0.50	[45]
		777	0.50	This work
	Liquid' + $\text{PuCl}_3 \rightarrow \text{RbPu}_2\text{Cl}_7(s_2)$	857	0.66	[45]
		857	0.66	This work
	$\text{RbPu}_2\text{Cl}_7 (s_1) \rightarrow \text{RbPu}_2\text{Cl}_7(s_2)$	647	n/d	[45]
		647	0.66	This work

2.6.3 Calculated phase diagram of the RbCl-CeCl₃ and the RbCl-PuCl₃ system

Phase equilibria temperature data from the heating cycles were highly reproducible, exhibiting variations of less than 1 K between onset and offset temperatures. In contrast, the temperatures of the DSC peaks within the cooling cycles showed greater variability, primarily due to supercooling effects, commonly reported in the literature for chloride and fluoride salts. Nonetheless, the cooling curves produced distinct sharp DSC peaks, which were particularly useful for identifying the number and characteristics of equilibrium transitions across the studied compositions.

Two phase equilibria datasets exist for the RbCl-CeCl₃ and one for RbCl-PuCl₃ system. Two CALPHAD optimisations of the RbCl-PuCl₃ systems have been published in recent years by Woei Jer Ng et al. (2023) [57] and by Huiqin Yin et al. [56] (2022), they have seemingly been able to reproduce well-fitting phase diagrams, yet some results are inconsistent. For instance, Yin et al. [56] incorporate low and high temperature allotropes of the Rb_3PuCl_6 and RbPu_2Cl_7 , yet their

calculated enthalpies of formation are seemingly two orders of magnitude lower than anticipated. Jer Ng et al. [57] $\Delta H_f^\circ(298.15\text{ K})$ values for intermediate compounds are in good agreement with this work, yet do not incorporate s₂ (β) allotrope for Rb₃PuCl₆ and its DSC measured enthalpy change.

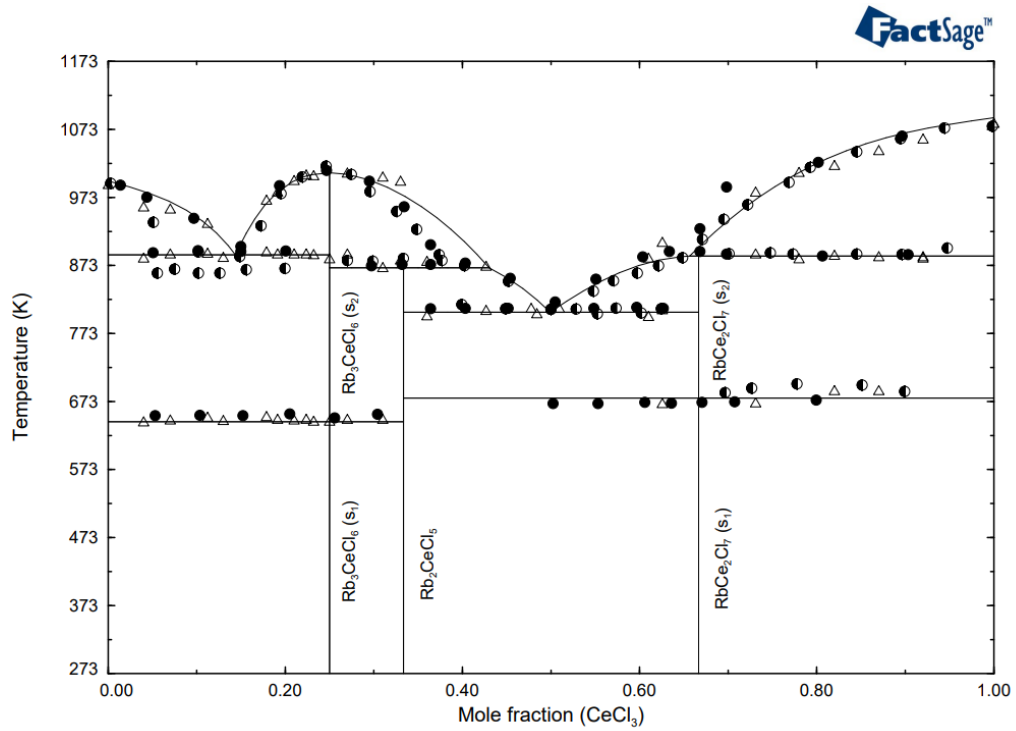


Fig. 2. 8: Comparison of the calculated RbCl-CeCl₃ phase diagram with the experimental data points from this work $\triangle$ (2025), $\bullet$ Seifert (1986) [43], $\bullet$ Gromov (1987) [42].

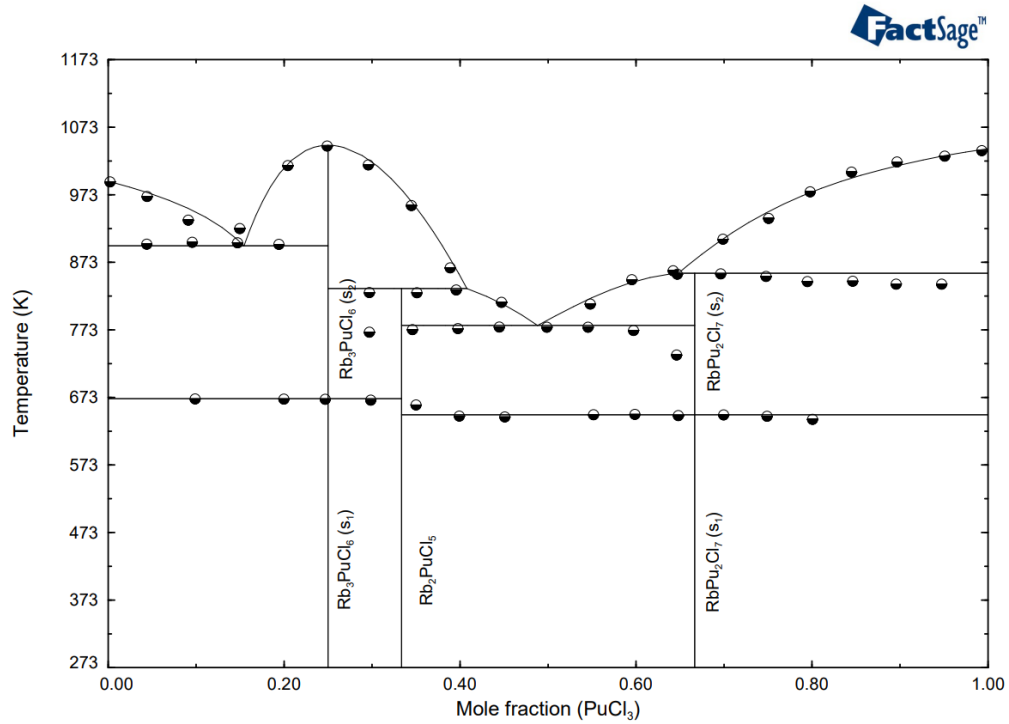


Fig. 2. 9: Comparison of the calculated RbCl-PuCl₃ phase diagram with the experimental data points ● from R. Benz (1961) [45].

2.6.4 Enthalpy of mixing

Understanding the enthalpy of mixing in molten salt solutions is essential, as it largely determines the overall Gibbs energy and strongly affects the system's redox potential (discussed further in **Section 5.6**). Experimental enthalpy of mixing data is available for the RbCl-CeCl₃ binary system; however, no experimental data currently exists for the RbCl-PuCl₃ system. Schorne-Pinto et al. (2022)[58] addressed this gap by employing a semi-empirical correlation method based on regression analysis, implemented in a Python 3.8 environment. Their approach yielded minimum enthalpy of mixing (ΔH^M) values that closely matched the available experimental data within two standard deviations across the broader AlkCl-PuCl₃ systems (where Alk = Li, Na, K, Rb, Cs), yet no emphasis was placed on the overall shape of the ΔH^M curve, which is implemented in this work. The calculated minimum ΔH^M for the RbCl-PuCl₃ system was $-19.606 \text{ kJ mol}^{-1}$ by Schorne-Pinto [58], while more negative values of $-20.1 \text{ kJ mol}^{-1}$ by Woei Jer Ng et al. [57], and $-20.3 \text{ kJ mol}^{-1}$ by Huiqin Yin et al.[56], while the present work yielded a value of $-19.2 \text{ kJ mol}^{-1}$.

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In the present work, a comparable ΔH_M value was independently computed using the linear methodology, but with added emphasis placed on preserving the overall shape of the curve that was produced by the data observed by Papatheodorou (1974) [40], particularly by maintaining a flatter and wider minimum. The approach reflects the hypothesis that two distinct coordination complexes, $[\text{PuCl}_4]^-$ and $[\text{PuCl}_6]^{3-}$, are likely to form at different compositions within the RbCl-PuCl₃ melt, analogous to the $[\text{CeCl}_4]^-$ and $[\text{CeCl}_6]^{3-}$ species confirmed by Raman spectroscopy in the RbCl-CeCl₃ system [40].

This hypothesis is further supported by the well-documented use of Ce as a surrogate for Pu in nuclear materials research, owing to their comparable physical and crystallographic properties. Notably, the ionic radii of Ce³⁺ and Pu³⁺ within chloride salts are nearly identical, reported at 0.101 nm and 0.100 nm, respectively. This similarity provides a strong rationale for the close agreement observed in binary phase diagrams and intermediate compound formation between alkali chlorides and their corresponding Ce and Pu trichloride systems.

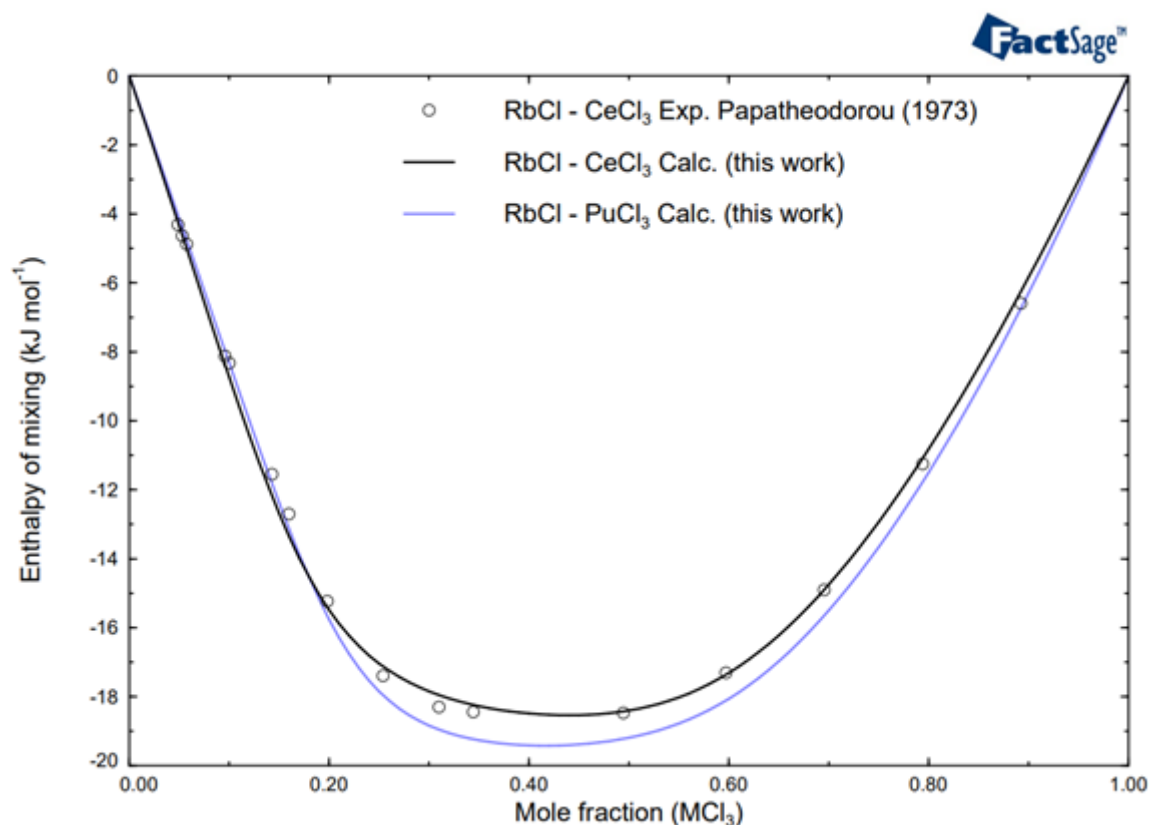


Fig. 2. 10: Calculated enthalpy of mixing of the RbCl-MCl₃ liquid solution, M = Ce, Pu. Temperature = 1118 K, ○ = Papatheodorou and Kleppa (1974) Exp. [40].

The enthalpy of mixing data, for both the experimental and calculated systems from different authors for the all systems are presented as a function of δ_{12} (Equation 2.4) below in **Fig. 2.11**. This further demonstrates the recalculated enthalpy of mixing in this work of the RbCl-CeCl₃ and RbCl-PuCl₃ systems that include the four and six-coordinated complex remain in very good agreement with the current literature.

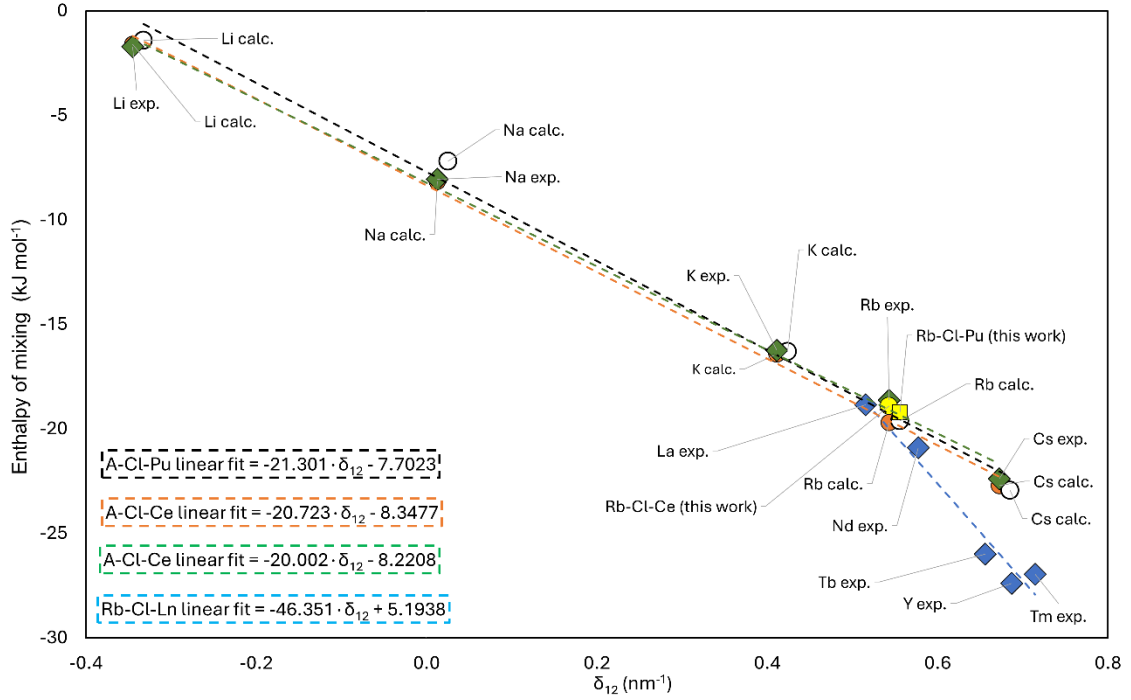


Fig. 2. 11: Experimental and calculated minimum enthalpy of mixing data of ACI-MCl₃ systems (where M = Ce, Pu; A = Li, Na, K, Rb) and δ_{12} as defined in Equation

4. ● ACI-PuCl₃ calculated by Schorne-Pinto et al. (2022) [58], ● ACI-CeCl₃ calculated by Schorne-Pinto et al. (2022) [58], ■ ACI-CeCl₃ measured experimentally by Papatherodorou and Kleppa (1973) [40], ■ RbCl-LnCl₃ experimental series; RbCl-LaCl₃ measured experimentally by Papatheodorou and Ostvold (1974)[39], RbCl-NdCl₃ measured experimentally by Gaune-Escard et al. (1994) [69], RbCl-TbCl₃ measured experimentally by Rycerz and Gaune-Escard (1998) [70], RbCl-YCl₃ measured experimentally by Papatheodorou et al. (1979) [71].

2.6.5 Liquid solution and short-range ordering

In this study, the liquid solution was modelled using the modified quasi-chemical model in the [71]quadruplet approximation (MQMQA), which accounts for short-range ordering among both first-nearest neighbours (FNNs) and second-nearest neighbours (SNNs) through the inclusion of quadruplet interactions, as outlined in **Section 2.5**. This study is the first of its kind for the RbCl-MCl₃ (where M = Ce, Pu)

systems introducing the Gibbs energies of the two complex species within the melt. The [MCl₄]⁻ and [MCl₆]³⁻ species represent pure liquid MCl₃ but were constrained by introducing entropic parameters that ensured constant complex compositions across all temperatures in pure liquid MCl₃ (as described by Eqs. 2.17-18 and 2.21-22). The larger Gibbs energy term represent in Eqs. 2.17 and 2.31 allowed the six-coordinated metal chloride complex to remain the dominant species in the RbCl rich-side solutions (**Figs. 2.12 & 2.13**), and the four-coordinated species to dominate in the RbCl dilute-side, as confirmed by Papatherodoru et al. [40].

To maintain thermodynamic consistency, a minor correction was introduced through manual iteration and uniformly applied to the standard Gibbs energy expressions of all complexes (Eqs. 2.17, 2.18, 2.21, 2.22). This adjustment was necessary to stabilise the system and bring the complexes into equilibrium with pure MCl₃ in both binary systems modelled in this work. Without this correction, the Gibbs energies of the Ce and Pu containing chloride complexes would have been excessively negative, resulting in an unrealistic thermodynamic dominance that would suppress the stability of Rb⁺ ions within the melt.

Table 2. 6: Liquid solution parameters for RbCl-CeCl₃ liquid solution Gibbs free energies g^o (J mol⁻¹)

$g_{Ce_{vi}Cl_3}^o = g_{CeCl_3}^o + 40.06740 \cdot (T/K)$	(2.17)
$g_{Ce_{iv}Cl_3}^o = g_{CeCl_3}^o + 0.06740 \cdot (T/K)$	(2.18)
$\Delta g_{RbCe_{iv}/Cl_2} = -16700 - 0.35 \cdot (T/K) - 4300 \cdot \chi_{RbCe_{iv}/Cl_2} - 1000 \cdot \chi_{Ce_{iv}Rb/Cl_2} + 4.2 \cdot (T/K) \chi_{Ce_{iv}Rb/Cl_2}^2$	(2.19)
$\Delta g_{RbCe_{vi}/Cl_2} = -30100 - 2.3 \cdot (T/K) \cdot \chi_{Ce_{vi}Rb/Cl_2} - 3.7 \cdot (T/K) \cdot \chi_{RbCe_{vi}/Cl_2} + 2500 \cdot \chi_{RbCe_{vi}/Cl_2}^2$	(20)

Table 2. 7: Liquid solution parameters for RbCl-PuCl₃ liquid solution Gibbs free energies g^o (J mol⁻¹)

$g_{Pu_{vi}Cl_3}^o = g_{PuCl_3}^o + 40.06792 \cdot (T/K)$	(2.21)
$g_{Pu_{iv}Cl_3}^o = g_{PuCl_3}^o + 0.06792 \cdot (T/K)$	(2.22)

$$\Delta g_{RbPu_{iv}/Cl_2} = -16900 - 6100 \cdot \chi_{Pu_{iv}Rb/Cl_2} - 2000 \cdot \chi_{RbPu_{iv}/Cl_2} + 10.0 \cdot (T/K) \cdot \chi^2_{Pu_{iv}/Cl_2} - 6.0 \cdot (T/K) \cdot \chi^3_{Pu_{iv}Rb/Cl_2} \quad (2.23)$$

$$\Delta g_{RbPu_{vi}/Cl_2} = -32000 - 3000 \cdot \chi_{RbCe_{vi}/Cl_2} + 4700 \cdot \chi_{RbPu_{vi}/Cl_2} + 2.1 \cdot (T/K) \cdot \chi^2_{Pu_{vi}/Cl_2} \quad (2.24)$$

Using these parameters, along with the thermodynamic data for the solid uranium- and rubidium-containing compounds provided in **Table 2.3**, the phase diagram shown in **Fig. 2.8 & 2.9** was calculated. The two eutectic points of interest were successfully reproduced, showing strong agreement with the new experimental DSC results presented in this study.

The standard Gibbs free energy functions of the cerium and plutonium complexes in the liquid phase are given in Eqs. 2.19, 2.20, 2.23 and 2.24. The larger correction term applied to the six-coordinated complex (Eqs. 2.17 and 2.21) suppresses its formation, resulting in the four-coordinated species becoming more dominant in the liquid solution at compositions where $X(MCl_3) > 0.21$, as also supported by Raman spectroscopy data. The SNN numbers highlighted in **Table 2.2** for the four and six-coordinated cerium and plutonium complexes forced maximum SRO at two different fixed compositions, for $[MCl_4]^-$ at $X(MCl_3) = 0.50$, $[MCl_6]^{3-}$ at $X(MCl_3) = 0.25$ where M = Ce, Pu in RbCl.

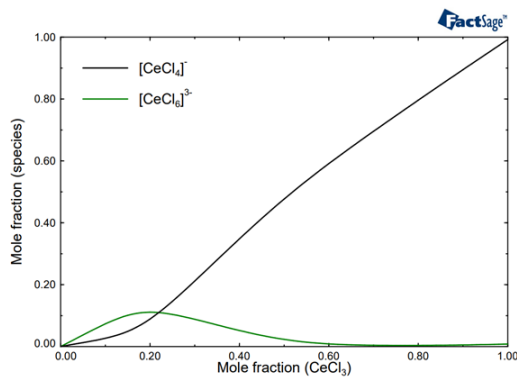


Fig. 2. 12: Mole fraction of cerium complexes in the RbCl-CeCl₃ system calculated in this work, T = 1118 K.

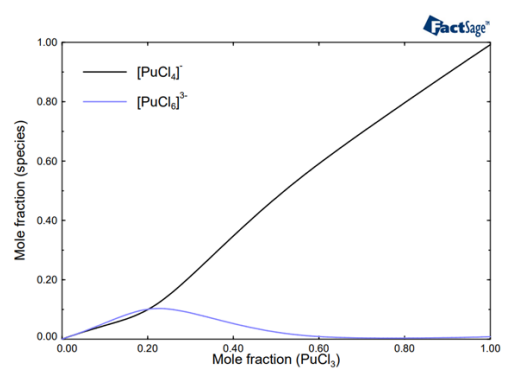


Fig. 2. 13: Mole fraction of plutonium complexes in the RbCl-PuCl₃ system calculated in this work, T = 1118 K.

2.6.6 Excess properties and activity

The determination of excess thermodynamic properties in molten salt mixtures constitutes a central objective of this study. Experimental data on the heat capacities of such systems remain scarce, with only a limited number of investigations addressing the variability of their thermophysical behaviour. In earlier work, Roger et al. (1982) [72] reported significant deviations in the measured heat capacities of the molten FLiNaK system (46.5 mol% LiF – 11.5 mol% NaF – 42.0 mol% KF) relative to values predicted by the Neumann–Kopp rule. A similar trend was observed in recent measurements of the heat capacity of molten FLiBe (66.7 mol% LiF, 33.3 mol% BeF₂) by Lichtenstein (2020) [73], further underscoring the limitations of additive models in accurately capturing the thermodynamic behaviour of complex molten salt systems. The FLiNaK and FLiBe solutions were measured without any actinide component(s). Limited studies have explored excess heat capacities including actinide salts, but Karlsson et al. (2025) [74] have identified that there is notable impact.

As shown in **Tables 2.6 & 2.7**, entropic parameters were introduced during the manual iterative modelling process in this work to accurately reproduce the phase diagram and capture the two eutectic points of the RbCl-MCl₃ system, while maintaining the enthalpic parameters necessary to represent the enthalpy of mixing for the liquid solution. The modelling also required the simultaneous refinement of the standard enthalpy of formation and standard entropy for three of the solid intermediate compounds to achieve thermodynamic consistency across all phases.

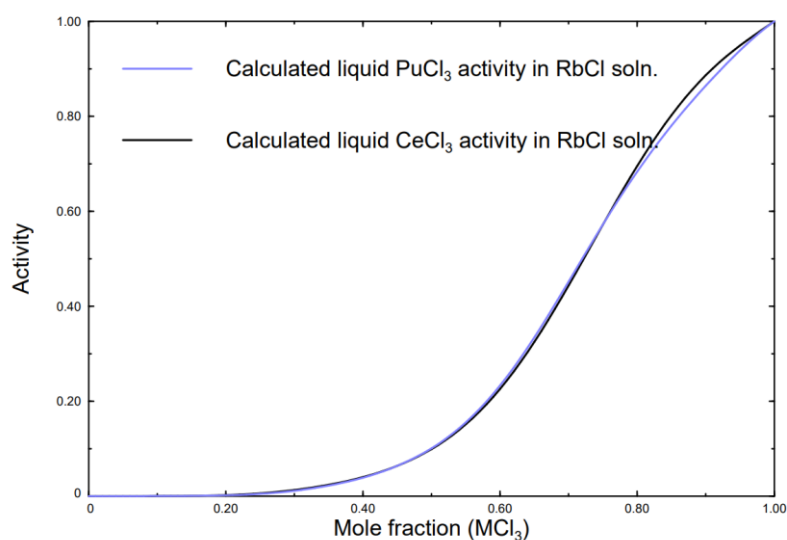
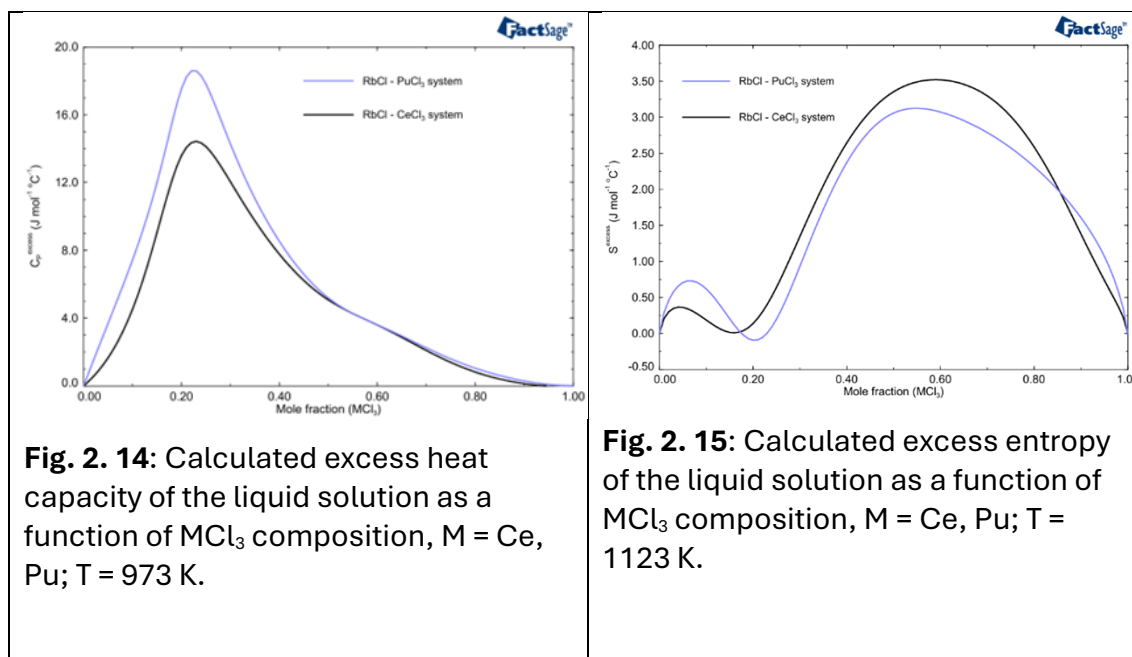
In contrast to the comparatively simple LiCl-KCl system, which exhibits a single eutectic point and no known intermediate compounds, solid solutions, or complex species in the liquid phase, the RbCl-MCl₃ system displays significantly greater complexity. This complexity primarily arises from the large differences in cationic charge-to-radius ratios (Z/r) between the two end-member components. Upon mixing, the ions in the molten lattice reorganise to achieve their lowest

configurational energy, giving rise to multiple intermediate phases and non-ideal solution behaviour.

The FactSage model calculates the corresponding excess terms (**Figs. 2.14 & 2.15**) based on the thermodynamic functions of the identified complexes, along with related properties such as activities (**Fig. 2.16**). The model reveals that the heat capacity of the system exhibits a distinct maximum at $X(\text{MCl}_3) = 0.22$ (**Fig. 2.14**), which may be advantageous for molten salt reactor (MSR) applications, particularly in smaller or more compact MSFR designs, where improved heat capacity can enhance thermal management.

These results are valuable because they identify compositions that exhibit the greatest degree of short range ordering, demonstrated by the minima in the excess entropies at $X(\text{MCl}_3) = 0.17\text{-}21$ (**Fig. 2.15**). This is also indicative of compositions that may be more likely to change phase and boil under extreme accident-type temperatures and scenarios. Such insights are crucial for fuel salt selection, as the stability or suppression of particular species within the melt that can influence corrosion behaviour and other undesirable chemical reaction pathways within the reactor environment.

Furthermore, **Fig. 2.16** shows that at $X(\text{PuCl}_3) = 0.5$, corresponding to the second eutectic composition, the activity of PuCl₃ remains non-zero. This indicates that, even at higher fissile loadings, PuCl₃ retains some thermodynamic activity and could potentially react with internal MSFR materials, with the extent of interaction governed by the chemical compatibility of the selected structural and functional components. They also indicate which chemical species in the molten salt are thermodynamically suppressed under equilibrium conditions.



2.6.7 Redox control and corrosion mitigation

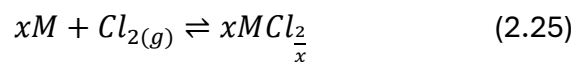
The migration of corrosion products is driven by gradients in Gibbs free energy, predominantly arising from thermally induced chemical potential differentials [75]. Consequently, a thermodynamic framework is essential for capturing the fundamental corrosion-driving forces in MSRs, necessitating the integration of

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rigorously defined thermodynamic models within multiphysics reactor simulation tools. In the MSRE, ORNL researchers identified redox potential control as essential for limiting alloy corrosion in molten fuel salts [76]. High-nickel alloys like Hastelloy-N were developed to replace stainless steels, which exhibited selective leaching of elements such as Cr, forming fluoride species in the salt. Cr was found in elevated concentrations in the salt and depleted at alloy surfaces. To suppress corrosion, the redox potential of the LiF-BeF₂-ZrF₄-UF₄ fuel salt was adjusted by adding UF₃, making the environment more reducing, an approach shown to be effective. Fission product, tellurium was also observed to migrate to the grain boundaries of the Hastelloy-N, causing significant embrittlement. While the exact mechanism of this was never fully understood, Keiser et al. (1977) [77] observed that is the redox potential of the LiF-BeF₂-UF₄ salt was low enough - with addition of UF₃ as the reducing agent - almost all Te intergranular cracking was effectively suppressed.

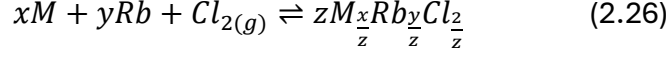
Although tri and tetra valent uranium chlorides are not the focus of this study, authors Fredrickson et al. (2018) [78] explore the importance of redox control of uranium chloride-based salt system by altering the ratio of UCl₄/UCl₃, yet do not discuss how the redox potential can significantly alter by simple addition of base salts such as AlkCl (where Alk = Li, Na, K, Rb). PuCl₄ has been difficult to isolate, and it is shown by calculation to be thermodynamically unstable [79]. If formed, it is likely that it would readily decompose back to PuCl₃ and Cl₂, making it unlikely to be one of the main MSFR fuel component, or to be mixed with PuCl₃ to control the redox potential.

One method to illustrate how the Gibbs free energy change of reactions between the alloying components and various salts versus temperature is through use of an Ellingham diagram. The Gibbs free energy change of these formation reactions per mol of Cl₂ (g) can be simplified as:



Where x are the stoichiometric coefficients to balance the reaction per mole of pure Cl₂ gas, M is metal element (M = Mo, Ni, Fe, Cr, Mn, U, Pu, Rb). Or in the case of the formation of the molten salt solution in this work:0

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Where y and z are additional stoichiometric coefficients to balance the reaction per mole of pure Cl₂ gas for the RbCl-PuCl₃ solution.

The Gibbs free energy of the forward reaction per mole of Cl₂ (g) in Equation 25 can then be written as:

$$\Delta G_r^\circ = xG_{MCl_{\frac{2}{x}}}^\circ - \left(xG_M^\circ + xG_{Cl_{2(g)}}^\circ \right) \quad (2.27)$$

Similarly for equation 26, the Gibbs free energy of the forward reaction per mole of Cl₂ (g) for the RbCl-MCl₃ solution:

$$\Delta G_r^\circ = zG_{M_{\frac{x}{z}}A_{\frac{y}{z}}Cl_{\frac{2}{z}}}^\circ - \left(xG_M^\circ + yG_A^\circ + xG_{Cl_{2(g)}}^\circ \right) \quad (2.28)$$

In this work, the newly modelled RbCl-PuCl₃ system, two compositions representing the two eutectics, 0.15 mol PuCl₃ soln. (85 mol% RbCl – 15 mol% PuCl₃) and 0.50 mol PuCl₃ soln. (50 mol% RbCl – 50 mol% PuCl₃) redox potential is plotted against other various salts including alloy corrosion product in **Fig. 2.17**:

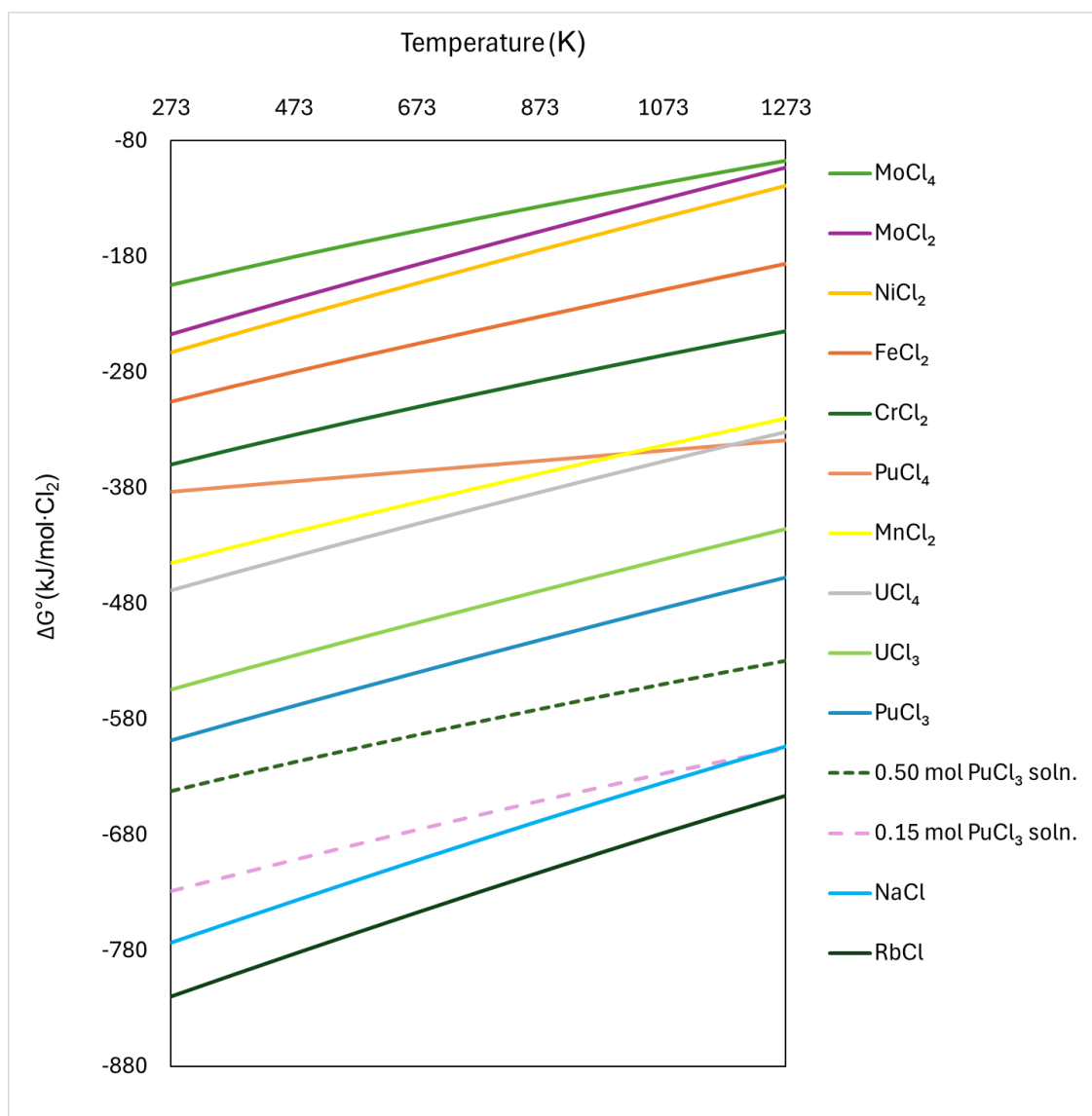


Fig. 2. 17: Standard Gibbs free energy of formation per mole of Cl₂ for salt components, corrosion products and molten salt solution (RbCl-PuCl₃ soln.) of the binary molten salt modelled in this work at composition $X(\text{PuCl}_3) = 0.15, 0.50$. Other data from Gurvich [68].

Pure PuCl₃, exhibits a more oxidising potential compared to the two eutectic compositions of the RbCl-PuCl₃ system. This indicates that both eutectic molten salt mixtures render the overall salt environment significantly more reducing. This is further illustrated by the absence of observable corrosion upon inspection of the mixture (88.8 mol% RbCl – 11.2 mol% CeCl₃) following the DSC experiment, as shown in **Fig. 2.4**. However, in MSFR configurations that operate without graphite moderation, issues such as uranium carbide formation, commonly associated

with highly reducing fluoride systems [23], are not relevant, as the absence of moderator materials could avoid this possibility entirely.

2.7 Discussion

Phase equilibrium temperatures in this study were determined from the onset and offset of DSC heating cycles (**Fig. 2.4**), as the heating data were more consistent. Cooling data were excluded due to supercooling effects, although the clearer peaks observed during cooling helped in identifying the number of equilibrium transitions for each composition. The phase equilibrium data reported here may offer greater precision and accuracy compared to the work of Seifert et al. [43] and Gromov [42], while generally remaining in agreement. This agreement validates the novel custom crucible design for thermal analysis of molten salts, whose sensitivity enabled detection of the Rb₃CeCl₆ polymorphic phase transition that Gromov [42] was unable to observe. These findings support the conclusions of L. Rycerz (2004) [39], indicating that Rb₃CeCl₆ undergoes a monoclinic Cs₃BiCl₆-type to high-temperature cubic elpasolite-type phase transition at 644 K, analogous to Rb₃PuCl₆ at 671 K - rather than attributing the observed thermal event to a formation reaction. The phase diagram presented by R. Benz [45] appears reliable and was corroborated through optical microscopy, which verified the solid intermediate compounds and their allotropes. However, experimental enthalpy of mixing data for the RbCl-PuCl₃ system would be valuable not only to confirm the minima but also to capture the overall shape of the curve, enhancing the reliability of modelling efforts. Potential considerations remain regarding the determination of types of crystal growth and their densities, which are important for anticipating the behaviour of solid phases during fuel fabrication or MSR cooling/shutdown scenarios.

Previous ORNL reports from the Aircraft Reactor Experiment (ARE) program [80], along with more recent literature reviews made by Kairos in collaboration with Argonne National Laboratory (ANL) [81], highlight the influence of cation-anion size ratios, often expressed as the charge-to-radius (Z/r) ratio, on molten salt behaviour. Deviations from ideal solution behaviour commonly arise from negative heats of

mixing, where the mixed salt possesses lower energy than the pure components, and can often form positive excess entropies associated with increased lattice disorder when dissimilar-sized cations are combined. Yet, it is possible to have decreased in excess entropy if ions undergo strong ordering under certain conditions with specific salt components and compositions. As reported in ORNL study [80], binary systems such NaF-ZrF₄ showed that the addition of UF₄ reduces the activity of ZrF₄, while simultaneously rendering it less stable relative to alkali fluoride (AlkF) mixtures. Yet, the reduction in ZrF₄ activity caused by UF₄ addition was less pronounced than that observed when decreasing the ZrF₄ concentration in the corresponding AlkF binary mixtures. This behaviour supports the concept that the thermodynamic stability of molten salt components in solutions can be, to some extent, explained by the effective Z/r ratio of the constituent ions.

A flexible molten lattice tends to converge toward the energetically most favourable ion configuration, enhancing electrostatic attractions and distorting the lattice, which often increases disorder - yet exceptions exist for strong SRO for specific salts systems and their respective compositions. These effects help explain why activity coefficients of pure end member components are frequently less than one (**Fig. 2.13**) at certain compositions. The more favourable energy configuration of dissimilar Z/r ions in solution may partly explain why more negative enthalpies of mixing are observed in heavier and larger AlkX systems across all experimentally studied AlkX-MX₄ and AlkX-LnX₃ binary systems (X = F, Cl, Br, I; M = Zr, Th, U) reported in the literature, when comparing systems within the same halide group. However, as noted in the Kairos-ANL [81] review, differences in Z/r ratio alone do not account for all non-ideal thermodynamic behaviour. ORNL [80] interpreted this by recognizing that additional fluorine ions supplied by UF₄ contribute to complex formation within the melt, also referred as; short-range ordering (SRO). The thermodynamic modelling in this study incorporates such behaviour through the inclusion of [PuCl₄]⁻ and [PuCl₆]³⁻ complexes, each dominating at specific PuCl₃ mole fractions within the RbCl melt. Complex formation within molten salt solutions can lead to significant deviations from ideal thermodynamic behaviour, particularly in systems containing cations with large differences in charge and ionic radius, e.g.,

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NaF-ZrF₄. Based on iterative thermodynamic modelling carried out in this work, our results suggest that the enthalpy of mixing is the dominant factor influencing the total Gibbs energy of the solutions and, consequently, the redox potential. Although complex formation has already been observed in the RbCl-CeCl₃ system via Raman spectroscopy [40], experimental validation should be performed for the RbCl-PuCl₃ system if it is selected as a fuel salt, either in a binary mixture or as part of a higher-order system.

The ORNL ARE report [80] further described molten salt mixtures in terms of their fluoroacidity. For example, in the NaF-ZrF₄ system, Na⁺ acts as the chloride donor (basic) while Zr⁴⁺ is the fluorine acceptor (acidic). In the RbCl-PuCl₃ system considered here, this would be described in terms of ‘chloroacidity’, Rb⁺ serves as the chloride donor (basic) and Pu³⁺ as the acceptor (acidic), forming species such as [PuCl₄]⁻ and [PuCl₆]³⁻. The combination of a stronger acid and a stronger base lead to more pronounced interactions upon mixing, which thermodynamically manifest as larger negative deviations from ideal solution behaviour. Rubidium’s tendency to donate its chloride ion to nearby uranium ions reflects its basic character and helps stabilise the molten salt mixture. The corresponding acid-base scale indicates that RbCl exhibits more basic character than LiCl, allowing predictions of deviations from ideal behaviour and relative solubilities. This approach may assist in selecting solvent compositions that promote the formation of stable complexes within the fuel salt, instead of alloy-component fluoride species, thus mitigating corrosion. Consistent with these principles, the RbCl-PuCl₃ system may exhibit higher melting points than the LiCl-PuCl₃ system. However, it is expected to provide greater corrosion resistance to structural alloys because RbCl more strongly stabilises actinide complexes rather than promoting the dissolution of alloying elements into the melt. This behaviour could potentially extend the operational lifespan of an MSFR. Similar conclusions were reached by Ocádiz Flores et al. (2021) [82], stated that reducing the total Gibbs free energy of the molten salt system enhances thermodynamic stability.

Other studies have shown that impurities can significantly influence salt corrosiveness, underscoring the need for further experimental validation of

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corrosion resistance improvements when incorporating heavier alkali chlorides. Interestingly, a recent study by Lucas et al. (2026) [83] further supports this hypothesis; in fluoride systems such as FLiNaK and FLiTh, the smaller (less negative) enthalpy of mixing between alkali fluorides, compared to LiF-ThF₄ as reported by Holm and Kleppa (1968) [84], corresponds to visibly reduced corrosion of SUS316L, based on purified samples after 3000 hours. Since MSFR designs do not employ graphite moderation, maintaining a strongly reducing environment eliminates the risk of uranium carbide formation and other adverse graphite interactions [85]. In addition to impurities, the MSRE program and researchers at ORNL identified fission product tellurium as a significant contributor to alloy degradation. They found that minimising Te-induced intergranular cracking under reducing conditions, through adjustment of the UF₃/UF₄ ratio could substantially enhance corrosion resistance, extend reactor service life, and yield favourable economic benefits. However, this introduces a trade-off, as excessive increases in UF₃ content can shift the salt chemistry too far towards reducing conditions, promoting graphite interactions and uranium carbide formation. Although tellurium-induced cracking was primarily observed in Hastelloy-N alloys developed at ORNL, McCoy (1978) [22] reported that SUS304 exhibited less Te cracking but showed increased chromium dissolution, all in contact with FLiBe salts.

This consideration highlights the importance of developing MSFR fuel salts that can remain highly reducing while simultaneously promoting the formation of stable complexes that suppress tellurium-induced intergranular cracking and minimise the dissolution of chromium and other alloying elements. In contrast to the MSRE, which employed fluoride salts and was constrained to use FLiBe due to its exceptionally low thermal neutron absorption - an essential property for achieving the reactor's goal as a thermal breeder - the MSFR operates in a fundamentally different neutron economy. This distinction opens opportunities to explore alternative salt chemistries. Accordingly, higher-order chloride systems incorporating RbCl and heavier alkali chlorides such as NaCl and KCl warrant further investigation, provided they maintain a low redox potential and exhibit other

desirable characteristics, including low melting points, high actinide and fission product solubility, and low vapor pressure.

2.8 Conclusions

For the first time, the RbCl-PuCl₃ system, identified as a potential fuel for molten salt fast reactors (MSFRs), has been thermodynamically modelled to account for the presence of four- and six-coordinated plutonium complexes in the melt and helps stabilise it more than lighter AlkCl-MCl₃ mixtures using RbCl-CeCl₃ system as surrogate system aiding in the identification of said complexes. These coordinated species were found to exhibit distinct ordering behaviours at two separate compositions, marking a novel approach in the thermodynamic description of such systems and will aid in building further higher-order system using the same approach.

Benefits include two eutectics at low temperatures and possible hardening of the neutron spectrum within an MSFR core using RbCl as the heavier atomic weighted carrier salt than LiCl, NaCl and KCl. CsCl, being heavier than Cs is monoisotopic (¹³³Cs) but its neutron absorption cross section is too large (2.5 + 26.5 b, yielding a safety relevant nuclide ¹³⁴Cs [86]) to be used as salt carrier in the fuel. This is not the case of Rb which occurs as (⁸⁵Rb and ⁸⁷Rb) but with small neutron absorption cross sections (0.06 + 0.45 b and 0.10 b, yielding no safety relevant nuclides [86]) to be used as salt carrier in the fuel. Furthermore, to optimise the neutron economy, ³⁷Cl can be separated from ³⁵Cl and used as suggested by and Deguelde & Merk (2023) [87].

In addition to neutronic advantages of salts with heavier atomic masses, the first eutectic at X(PuCl₃) = 0.15 may offer lower corrosion but has a higher temperature and less fissile loading. The second eutectic at X(PuCl₃) = 0.50 allows higher plutonium loading in the fuel - expanding the possibilities of smaller and more compact MSFR cores for applications including, but also outside electricity production in conventional thermal power plants.

While UCl₃ is widely recognized as a key component [88] in the initial fuel composition of a molten salt fast reactor (MSFR), PuCl₃ represents a viable alternative BOL fuel source and long-term fuel source, particularly relevant if the United Kingdom opts to utilise its stockpile of approximately 140 tonnes of plutonium at Sellafield. Regardless of MSFR design (i.e. burn, converter or breed-type), as the fission process proceeds, neutron capture by ²³⁸U will inevitably produce some Pu, but in its most stable form within fuel molten matrix; PuCl₃. This transmutation pathway is especially important if MSFR designs incorporate breeding zones or "blankets" intended to extend fissile material availability and enhance long-term energy security. Ce is a notable fission product, and the updated model developed in this work, which includes its complex formation behaviour, is relevant even when used as a surrogate. This model will be valuable for future thermodynamic studies involving RbCl in MSFR applications.

This study highlights the critical need for accurate and robust methodologies in determining thermodynamic properties, particularly in systems where experimental data are scarce or unavailable. By optimising DSC through the use of ultra-low-mass, corrosion resistant and hermetically-sealed crucibles, thereby enhancing thermal sensitivity and by extending the Gibbs free energy functions to include plutonium and cerium based multi-coordinated complexes in a RbCl melt, this work establishes a reliable framework for thermodynamic modelling using minimal sample quantities, effectively reducing material consumption and waste.

As molten salt nuclear technology continues to advance, the findings presented here lay an essential foundation for future investigations into plutonium and other actinide-based salt systems, thereby contributing to the development of advanced fuel cycles and next-generation molten salt reactor (MSR) designs.

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Chapter 3: The first thermodynamic investigation and optimisation of the RbCl-UCl₄ system: a potential reciprocal salt system for the molten salt fast reactor

3.1 Abstract

Thermodynamic properties of the RbCl-UCl₄ system, a potential reciprocal salt system for Molten Salt Fast Reactors (MSFR), have been investigated for the first time combining experimental data gained by Differential Scanning Calorimetry (DSC) through use of the novel crucible developed at Lancaster University and modelled with the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA). This binary system is known to have a high vapour pressure due to its thermodynamic properties deviating far from ideal simple molten salt mixtures while sharing the same chloride anion. The significance of UCl₄ as a salt component in thermodynamic optimisations is to accurately predict the evolution of properties as the starting fuel component; UCl₃ is oxidised throughout the fission reaction process in an operational MSFR. The RbCl-UCl₄ system exhibits strong ionic interactions due to short range ordering (SRO), and the two intermediate compounds of relatively low thermal stability allow for low melting temperatures with high UCl₄ solubility and large excess heat capacity for a smaller more compact MSFR core design. This binary system will allow for subsequent higher order systems to be modelled for potential starting fuel for molten salt fast reactors with favourable neutronics. This work is the first of its kind for phase diagram exploration and full thermodynamic characterisation focusing on Rb cation in the solution.

3.2 Introduction

Molten salt reactors are a branch of nuclear technology that has recently seen a large resurgence in attention across the world in both national governments and private companies [89]. Originally researched and developed in the 1950s and 60s in the U.S. as prototype and demonstration scale reactors, their liquid fuelled core

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provides large differences in operation, uses and safety than their solid fuelled cousins at the time. By the end of the 60s, research and development was halted due to a combination of decisions, mainly political, and since then, there has been no urgent requirement for such a technology to exist at the commercial scale. Other reactors in operation to date, such as the Pressurised Water Reactor (PWR) technologies have dominated the sector – thanks to their high reliability, but all using solid uranium dioxide fuel pellets, with slight variations in reactor geometry, design and materials to produce exclusively electricity with very few exemptions using low temperature waste heat to supply district heating networks.

Nowadays, there is an expected exponential increase in growing energy requirements to fill demand from electricity and heat to power new and more sustainable industries. The large global scientific consensus on climate change also puts additional stress on politicians and policy makers to fill the gap without extensive extraction, refinement and combustion of fossil fuels. With renewables energy technologies such as solar and wind making impressive strides in capacity deployment on an annual basis, their overall generation dwarves that of continued growth of fossil fuel-based generation that still dominates electricity generation, barely penetrating transportation and industrial sectors. This is partly why we have seen a second look to MSR technology as they can provide a compelling solution to many of the energy challenges that near-future societies face. MSRs not only could provide electricity, but direct high temperature heat to drive many industrial processes and synthetic fuel production for use in many sectors that are difficult to electrify, such as transport [90].

This work focuses on the sub-category within the MSR realm, known as Molten Salt Fast Reactors, which use no moderating component inside the reactor. Typically, the vast majority current operational reactors use a moderating material, such as water to slow neutrons to a ‘thermal’ speed $\sim 0.0025\text{eV}$ which makes a fission reaction of uranium far more probable. The main downside of thermal neutrons is that when they do not induce fission, the uranium atom instead ‘captures’ the neutron, transmuting into heavier elements and their respective isotopes, thus ensuring a small build-up of higher actinides such as plutonium, neptunium,

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americium and their isotopes. Some of these elements isotopes are seen to be more troublesome than the fission products of uranium as they typically have far longer half-lives which raises some concern for geological repositories for spent fuel. For example, ²³⁷Np has a half-life of 2.14 million years, whereas ¹³⁷Cs is 30.17 years, and so after ~300 years, only 0.1% will remain inside spent nuclear fuel. The difference for fast-neutrons is that they are about 40 million times more energetic, at >1 MeV, they are not captured by the heavier actinides and fission them all, which, in theory, could leave the waste stream of a fast reactor only consisting of pure fission products – some of which can be used for radiopharmaceutical applications, as reported by Degueldre *et al* (2024) [18].

Of course, the main drawback of implementing fast reactors is that they need a larger initial fissile load of ²³⁵U and/or ²³⁹Pu to maintain the nuclear fission reaction within the core, as fast neutrons are less probable to induce fission than thermal speed neutrons. A compensating factor for this reduced fission probability is that fast neutrons, when they do induce fission in an actinide nucleus, yield a higher average number of neutrons per fission, thereby significantly increasing the neutron flux within the core. The higher neutron flux, combined with fast fissioning of all actinide isotopes, increases the burn-up relative to a thermal reactor, allowing more energy to be extracted per unit mass of fuel, hence why MSFRs could be said to be more sustainable. Regarding the sustainability of nuclear energy, coupling a nuclear power plant's cooling system to extract uranium from seawater, by definition, would make fast reactors renewable, see Degueldre (2017) [91] and its use in a Molten Salt Fast Reactor as reported by Degueldre *et al* (2019) [92].

Fast reactors can also be configured to 'breed' more fuel than they consume, often termed, 'breeder' reactors. This happens due to the excess neutrons from the core being captured in an outer region termed the 'blanket' of non-fissile ²³⁸U, which transmutes to ²³⁹Pu, which is fissile. Although being expressed as a proliferation concern, this would dramatically increase the amount of potential energy that could be extracted from natural uranium that is currently mined. Seeing as thermal reactors are only able to exploit the ²³⁵U, which only makes up 0.7% of natural uranium, typically enriched to ~5% or less. This could ensure energy security for

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many countries already with uranium and spent fuel stockpiles. As explored by M. Taube (1977) [16], MSFRs can be designed specifically to have zero plutonium output, and to fission all fissile and non-fissile higher actinides – also simultaneously enabling far longer periods without refuelling, which could be more suitable for countries with less political stability.

Few fast reactor programs have been successful, and many other quickly developing countries are pursuing multiple stage reactor programs to ensure energy security in the long term, but no MSFR has been built or operated to date. A MSFR had been first assessed in the UK in 1974 by Smith et al [93], however, the resurgence in interest due to the rapidly rising energy requirements and energy security, the MSFR is having extensive research and development being undertaken in the U.S. at both the federal level and private equity. Needing no moderator or fuel assemblies in the core, the MSFR is a vessel filled with liquid molten salt fuel, in a specific geometry that enables a self-regulating nuclear fission reaction – reducing complexity of the internal configuration of the reactor and the need to shut down for refuelling.

Since an MSFR would have little-to-no solid components, fuel assemblies or moderating materials within the core, the fuel composition itself primarily determines the neutronics and neutron economy. Using salts containing ionised atoms with heavier atomic weight, such as Rubidium and Chloride, limits moderation and thus fast neutron speeds are more easily maintained – essential for successful MSFR operation, and the foundation of the work presented here. This work is some of the first that has enabled the construction of the RbCl-UCl₄ phase diagram and its thermodynamic optimisation to calculate its thermochemical properties of interest of all compositions and varying temperature in both the solid and liquid phase. It presents the results from Differential Scanning Calorimetry (DSC). Utilising the modified quasi-chemical model quadruplet approximation (MQMQA) which, unlike other models, is used to describe solid/liquid mixtures, incorporates Gibbs free energy exchange of the degree ‘short-range ordering’ of the various ions and complexes within the molten mixture due to their

differences in ionic charges and radii. Through careful Gibbs energy optimisation of this binary system through MQMQA model, we gain other insights to other thermodynamic properties such as excess entropy, chemical activity and heat capacity.

3.3 Thermodynamic considerations and overview

3.3.1 Thermodynamics of solutions

Computational models are required to calculate the chemical equilibrium, reaction kinetics, transport properties and thermochemical behaviour of complex multicomponent multiphase systems. This often become more complicated as the multicomponent and multiphase systems change with composition over time – as what will occur in an MSFR as the fission reaction progresses and uranium ions within the bulk fuel solution are fissioned into completely new fission product isotopes. Experimental data is required as input for the model parameters, yet most data do not exist, or experiments are too complex to be carried out for extraction of said parameters. Therefore, to enable predictions in more complex multicomponent multiphase systems, robust thermodynamic descriptions of simpler systems are essential. The computational models are based on Gibbs free energy minimisation, which is calculated using modern software, in this case, Factsage. That said, for multi-component systems, thermodynamic data is firstly taken from pure end-member components, relevant experimental data and the interaction parameters.

Solution phases' thermodynamic properties must be established as a function of composition and temperature to calculate phase equilibrium and other possible chemical reaction pathways that involve the solution. For this reason, many thermodynamic models have been developed to describe various organic and inorganic solutions for solid, liquid and gas phases. It is important to note that the gas phases are completely miscible, but solid and liquid phases can exhibit common phase separation, i.e. immiscibility. Non-ideal gas behaviour can be modelled in various ways; however, in this work, under the high temperatures (>400°C) and ambient pressures typical of an operational MSFR, gas models are not

accounted for. These effects should be evaluated and incorporated in future studies if the liquid solution properties prove promising for an MSFR fuel and design. Generally applicable to all solution phases, the Gibbs energy is given by the formula:

$$G = G^\circ + \Delta G_{mix}^{ideal} + \Delta G_{mix}^{excess} \quad (3.1)$$

Where G° is the Gibbs energy of the pure components within the solution phase of interest, ΔG_{mix}^{ideal} is the ideal Gibbs energy of mixing and ΔG_{mix}^{excess} is the excess Gibbs energy of mixing that introduces the non-ideal contributions into the solution.

Gibbs energy minimisations are performed computationally for complex systems and can determine true chemical equilibrium once the data from all phases are input into the model. The Gibbs energy is hence described as:

$$G = \sum_i n_i \bar{G}_i \quad (3.2)$$

Where n_i is the number of moles of component i , and $\bar{G}_i$ is the calculated or known chemical potent of component i , for a given set of fixed constraints, such as P , T and overall composition. In Section 4, the framework of the relevant thermodynamic model used to best describe molten salt solutions that exhibit Short-Range-Ordering (SRO) is further explained.

3.3.2 Standard enthalpy and entropy of solid intermediate compounds

Within the RbCl-UCl₄ system, there are only three solid intermediate compounds reported by Konings (2010) [79]. These are Rb₄UCl₈, Rb₂UCl₆ and RbUCl₅ with their standard enthalpy of formation at 298.15K reported and their standard entropy not given within this text. One other mention of the solid intermediate compounds of this system; Rb₃U₂Cl₁₁ and RbU₃Cl₁₃ are reported to melt incongruently by Morss (2011) [79] but no further references or information is given. These were used in the first iterations of the phase diagram optimisation, but even manually altering the standard entropy significantly, they could not be stabilised to reproduce the DSC data presented in this work. The analysis of the DSC heating data also suggested

one eutectic directly at the composition of Rb_4UCl_8 , so it was discarded. The Factsage 8.3 software was used to calculate the first iteration of standard enthalpy of formation and the standard entropy of Rb_2UCl_6 and RbUCl_5 through Neumann Kopp (NK) rule that is also applied to C_p calculation for these intermediate compounds. The first iteration involves stabilising them in the liquid phase at a given composition and temperature as the liquid phase's properties were introduced prior to first calculations. The standard procedure was to calculate the chemical activities of the compounds that melted congruently at known temperatures first, then compounds with incongruent melting after. As the Factsage software calculates the Gibbs energy of the liquid phase at same composition and temperature of the congruently melting compound, from the enthalpy of mixing data that was known experimentally or estimate by calculation from similar molten salts for which experimental data that does exist using ionic radii. At these conditions, the Gibbs energy of the liquid phase and the compound must be equal as they are in equilibrium. To stabilise the congruently melting compound in the liquid, with chemical activity > 1 , Eq. 3.3 was used whilst maintaining the standard entropy at the NK estimation:

$$\Delta H_{298.15K}^\circ = \Delta H_{298.15K}^\circ(\text{NK}) + R \cdot T \cdot \ln(a) \quad (3.3)$$

Where R is the gas constant, T is the temperature of the eutectic or congruent melting, and a is the chemical activity of the compound that has yet to be stabilised, calculated in the *Factsage Equilib* module.

The Gibbs energy at the temperature of interest is then fixed, i.e. at the congruent melting point of the eutectic, then the newly stabilised value of $\Delta H_{298.15K}^\circ$ and $S_{298.15K}^\circ$ can be simultaneously altered to reproduce the solidus and gradient of the slopes of the liquidus. This is typically more straightforward for the congruently melting compounds, for the compounds that form eutectics, special care was taken to calculate the activity of the un-stabilised compounds as specific molar ratios in the *Factsage Equilib* module but was found to reproduce accurate eutectic compositions and temperatures. Lastly, for compounds that melted incongruently, a process of multiple iterations were used to stabilise the compounds to reproduce

the best fits of the experimental phase diagram data whilst simultaneously introducing the excess entropic parameters into the liquid solution.

3.3.3 Enthalpy of mixing

No experimental data for the RbCl- UCl_4 system exists for the enthalpy of mixing, neither do many for alkali metal halides – uranium equivalent tetrahalides or RbCl-Actinide tetrachloride mixtures. Therefore, the linear prediction method as a function of ionic radii parameters proposed by Robeline et al (2011) [55] could not be used for a calculation. In a more recent publication made by J. Flores et al (2022) [82], a calculation of AlkCl- ThCl_4 mixtures were made, where Alk = Li, Na and K. The enthalpy of mixing of the ThCl_4 containing mixtures were presented in that work that may serve as another dataset, but it not clear how they were obtained (i.e. through Optisage software or a similar manual iterative method in this work), they do follow the same trends seen in other tri and tetra valent fluoride and chloride containing salt systems which have been measured experimentally. The experimental ΔH^{mixing} datasets that exist for AlkF- ZrF_4 , AlkF- UF_4 , and AlkF- ThF_4 , as well as the calculated AlkCl- ThCl_4 data, were plotted as function of ionic radii δ_{12} parameter. The δ_{12} parameter is defined as:

$$\delta_{12} = \frac{[r_A^+ + r_X^-] - [r_M^{4+} + r_X^-]}{[r_A^+ + r_X^-] - [r_M^{4+} + r_X^-]} \quad (3.4)$$

Where r_A^+ is the ionic radius of the alkali cation in the systems, r_M^{4+} is the ionic radius of the tetravalent metal cation and r_X^- is the ionic radius of fluorine or chloride in each binary system. An assessment of existing ΔH^{mixing} datasets as a function of δ_{12} (demonstrated in **Fig. 3.9**) confirmed the presence of a comparable trend. One trend common to all mixtures, including AlkX - MX_3 , where Alk = Li, Na, K, Rb, Cs and X = F, Cl, Br, I binary systems, that with heavier Alk cation, i.e. $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$, the more negative the ΔH^{mixing} . However, there is also overlap when varying the halide anion, as changes in charge-to-ionic radius ratio affect the system - which is discussed and shown later in this work. These correlations were then used to give a first estimate for the AlkCl- UCl_4 of the ΔH^{mixing} . In an initial assumption that ΔH^{mixing} of AlkCl- UCl_4 systems were more negative than that of J.Flores' proposed AlkCl- ThCl_4 equivalent alkali cationic systems, similarly to that the experimental ΔH^{mixing}

values of the AlkF-UF₄ systems are more negative than the experimental ΔH^{mixing} values AlkF-ThF₄ equivalent systems, gave highly negative Gibbs energy of mixing of the liquid solution. For this sensitivity analysis-based iteration, these ΔH^{mixing} values were discarded as $\Delta H^\circ_{298.15K}$ of Rb₂UCl₆ and RbUCl₅ that enabled them to be stable at given temperatures deviated significantly from the values given by Konings (2010). It should be noted that, once the $\Delta\delta_{12}$ values are calculated, larger differences in these values for equivalent MX₃ or MX₄ systems, with the alkali halide held constant, for example comparing NaF-ThF₄ to NaF-ZrF₄ or KCl-LaCl₃ to KCl-TmCl₃, correspond to greater variations in ΔH^{mixing} . This behaviour arises from increasing mismatches in ionic radii. Accordingly, additional care was taken to ensure that the values followed consistent trends, not in terms of absolute gradient, but in their relative increase when progressing to heavier alkali halides. However, the sensitivity analysis results published in this work gave rise to $\Delta H^\circ_{298.15K}$ values of the intermediate compounds that were more in line with Konings *et al.* (2010) [79] – for this reason the Gibbs energy functions of the liquid that kept ΔH^{mixing} at these values were kept.

One other important consideration was given when estimating the ΔH^{mixing} , for all experimental calorimetric studies on the AlkF-MF₄ (Alk = Li, Na, K; M = Zr, Th, U) there is minimum at X(MF₄) = 0.4. Plotting as a function of λ^{mixing} , in other calorimetric studies reveals indication of specific complex species within the melt.

3.3.4 Crystallographic data

The crystallographic data of compounds are essential for understanding their structural and physical properties. These data provide insights into the atomic arrangement, space groups, and lattice parameters, which are essential for phase diagram assessments. In this study, two end member compounds (RbCl and UCl₄) and two intermediate compounds (Rb₂UCl₆ and RbUCl₅) within the UCl₄-RbCl binary system; Rb₄UCl₈, Rb₂UCl₆, RbUCl₅, Rb₃U₂Cl₁₁ and RbU₃Cl₁₃ are reported in literature. Some crystallographic and enthalpy of formation data are reported in ‘The Materials Project’ [94] and ‘Open Quantum Materials Database’ [95]. For the end member compounds RbCl and UCl₄, the data are easily available at room temperature. **Table 3.1** summarizes the data from the end members and complexes investigated.

Table 3. 1: Crystallography data of the end members of the RbCl-UCl₄ system and their intermediate compounds.

Chloride	RbCl mol%	<i>M</i> g mol ⁻¹	Space group	ρ g cm ⁻³	Ref
RbCl	100.00	120.921	<i>Fm</i> $\bar{3}$ <i>m</i>	3.05	[33]
Rb ₂ UCl ₆	66.67	621.682	<i>C2/m</i>	3.76 ()	[95]
RbUCl ₅	50.00	500.762	<i>n/a</i>	n/a	-
UCl ₄	0	379.841	<i>I4</i> ₁ / <i>amd</i>	6.02	[95]

3.4 Thermodynamic data for compounds

The thermodynamic data ($\Delta H^\circ_{298.15K}$, $S^\circ_{298.15K}$ and C_P) for all compounds are optimised in this work and are given in Table 2. The molar Gibbs free energies of these compounds are expressed as:

$$G(T) = \Delta H^\circ_{298.15K} - T \cdot S^\circ_{298.15K} + \int_{298.15K}^T C_P dT - T \int_{298.15K}^T \frac{C_P}{T} dT \quad (3.5)$$

Where $\Delta H^\circ_{298.15K}$ is the standard enthalpy of formation, $S^\circ_{298.15K}$ is the standard entropy of formation at 298.15K and C_P represents the isobaric heat capacity. To be consistent with NIST-JANAF, the standard state pressure refers to 1 bar. It is standard practice that an empirical polynomial equation is used to describe the C_P :

$$C_p = a + bT + cT^2 + dT^{-2} \quad (3.6)$$

Where a , b , c and d are unitless empirical constants for given temperature ranges shown in **Table 2** for pure end-members and calculated coefficients by NK method for intermediate compounds in this study.

3.4.1 Thermodynamic data of pure UCl₄

In this work, data was taken from the Factsage database FactPSBASE, data is from Barin (1995) [44], which for UCl₄ (s) uses -1019.20 kJ mol⁻¹ for $\Delta H^\circ_{298.15K}$, 197.10 J mol⁻¹ K⁻¹ for $S^\circ_{298.15K}$, a C_P function shown in **Table 3.2** and a ΔH^{fus} of 45.606 kJ mol⁻¹. The

same dataset used for liquid UCl_4 uses $-976.37 \text{ kJ mol}^{-1}$ for $\Delta H^\circ_{298.15\text{K}}$, $246.28 \text{ J mol}^{-1} \text{ K}^{-1}$ for $S^\circ_{298.15\text{K}}$. Comparing data to the only other Factsage database with UCl_4 , SGPSBASE, data from Gurvich (1994) [68] recorded have very similar C_p functions (shown in **Fig 3.1.**) and almost identical Gibbs energy functions – for this reason, no alterations or modifications were deemed necessary.

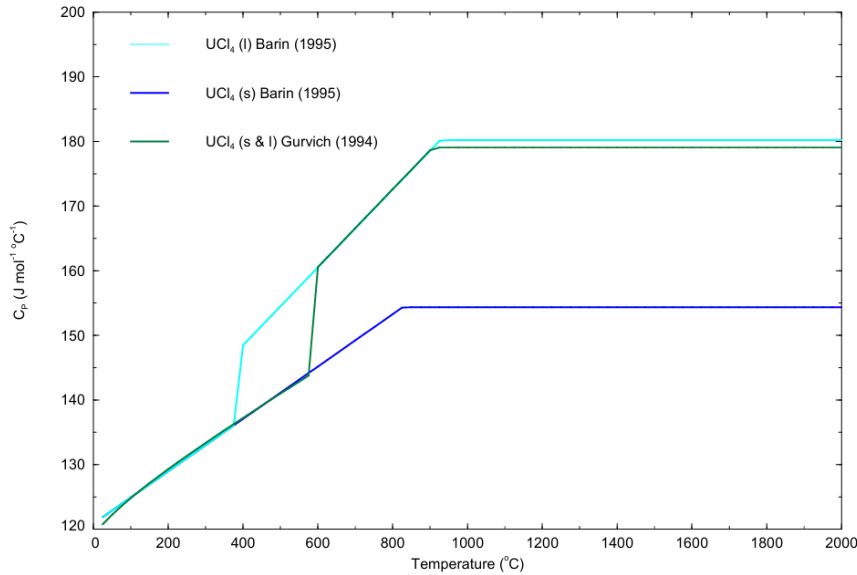


Fig. 3. 1: Pure UCl_4 C_p functions for solid and liquid from two Factsage thermodynamic databases.

3.4.2 Thermodynamic data of pure RbCl

RbCl containing salt systems have received little interest for molten salt reactor fuel candidates. Due to all intermediate compounds of the RbCl-UCl_4 system have melting points or decomposition temperatures below the melting point of RbCl (720°C), less careful consideration was given to the C_p of the solid phase, as this would be used in the Neumann Kopp method in part for determining the C_p of the all other compounds. C_p of RbCl of the solid phase was remodelled slightly to plateau at higher temperature alongside the liquid C_p . As one of the eutectics of the RbCl-UCl_4 system in the RbCl rich side was as low as 427°C , the liquid C_p by Gurvich (1994) [68] was not remodelled and kept constant, for future ternary systems where ternary eutectic are expected to be even further below 427°C (**Fig. 3.2**).

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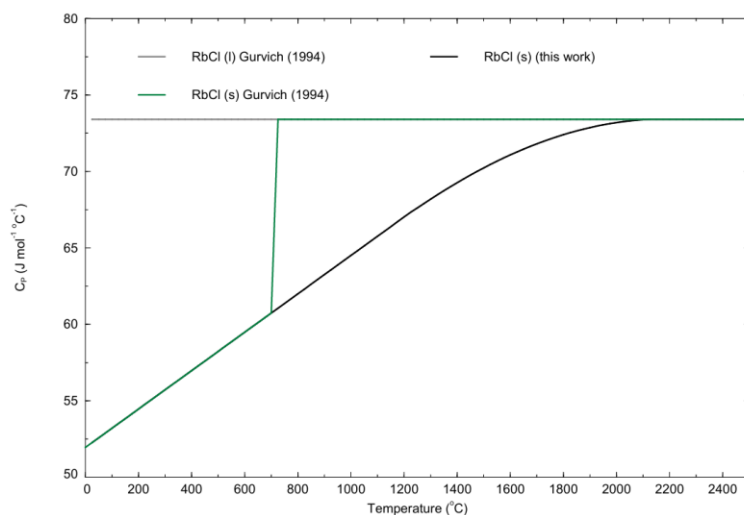


Fig. 3. 2: Pure RbCl liquid and solid C_P remodelled in this work.

3.4.3 Intermediate compounds

The thermodynamic data of the end members of the RbCl- UCl_4 system and their intermediate compounds are reported in **Table 3.2**. For the end member data are known for the solid and liquid materials while for the intermediate compounds data are only known for the solid phases.

Table 3. 2: Thermodynamic data of the end member RbCl- UCl_4 and their intermediate compounds.

Compound	T range (K)	$\Delta H^\circ_{298.15\text{K}}$ ($\text{J}\cdot\text{mol}^{-1}$)	$S^\circ_{298.15\text{K}}$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	C_P ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	Ref.
$\text{UCl}_4(\text{s})$	298.15-1100	-1019201.0	197.10	$109.8 - 0.0405 \cdot T$	Gurvich (1994) [68]
	1100-2500			154.35	
$\text{UCl}_4(\text{l})$	298.15-650	-976372.706	246.277	$109.8 - 0.0405 \cdot T$	
	650-1200			$107.9 - 0.06025 \cdot T$	
	1200-3000			180.2	
RbCl(s)	298.15-1500	-435220.0	95.23	$48.51268 + 0.01256576 \cdot T + 95.11015 \cdot T^{-2} - 3.80492\text{E-}9 \cdot T^2$	This work
	1500-2400			$25.05421037 + 0.037889418 \cdot T + 5533098.364 \cdot T^{-2} - 7.55943\text{E-}6 \cdot T^2$	
	2400-3400			73.4	

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RbCl(l)	298.15-3400	-422526.771	98.44	73.4	
Rb ₂ UCl ₆ (s)	298.15-1100	1988433.202	386.56	$206.82536 + 0.06563152 \cdot T + 190.2203 \cdot T^2 - 7.60984E-9 \cdot T^2$	(This work)
	1100-1500			$251.37536 + 0.02513152 \cdot T + 190.2203 \cdot T^2 - 7.60984E-9 \cdot T^2$	
	1500-2400			$204.45842074 + 0.075778836 \cdot T + 11066196.728 \cdot T^2 - 1.511886E-5 \cdot T^2$	
	2400-3400			301.15	
RbUCl ₅ (s)	298.15-1100	1513044.114	280.33	$158.31268 + 0.05306576 \cdot T + 95.11015 \cdot T^2 - 3.80492E-9 \cdot T^2$	(This work)
	1100-1500			$202.86268 + 0.01256576 \cdot T + 95.11015 \cdot T^2 - 3.80492E-9 \cdot T^2$	
	1500-2400			$179.40421037 + 0.037889418 \cdot T + 5533098.364 \cdot T^2 - 7.55943E-6 \cdot T^2$	
	2400-3400			227.75	

3.4.4 Thermodynamic modelling of the liquid phase

The modified quasi-chemical model quadruplet approximation (MQQA), proposed by Chartrand et al (2001) [28] was used to model the excess Gibbs energy of the liquid phase. The quadruplet model consists of two sub-lattices, one consisting of cations A and B (representing U⁴⁺ and Rb⁺) and anion F⁻ (in this work only fluoride anion is present). The quadruplet is the fundamental unit in this model. In previous models, i.e. QCM pair approximation, the first-nearest neighbours (FNN) interactions rather than the second-nearest neighbours (SNN) were modelled to be the dominant influence on the excess terms, shown in **Fig. 3.3**. The quadruplet approximation is updated and treats FNN and SNN interactions simultaneously for determining optimised excess parameters of the liquid solution.

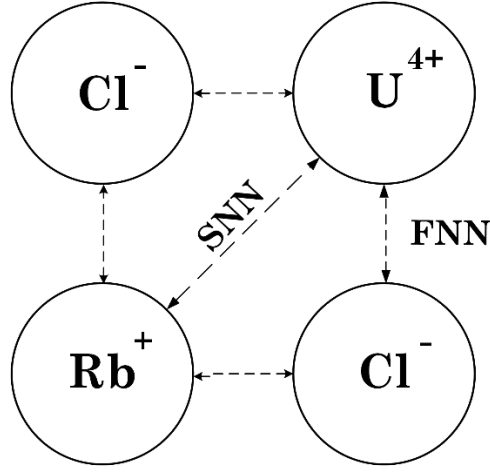
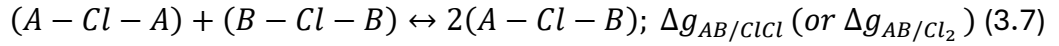
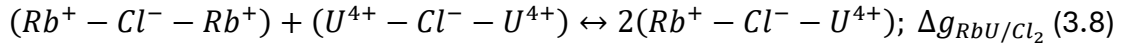


Fig. 3. 3: Schematic of one quadruplet model illustrating first-nearest neighbour (FNN) and the second-nearest neighbour (SNN) with two cations (Rb⁺) and (U⁴⁺) and two anions both (Cl⁻) in this case.

The transfer reaction between FNN and SNN pairs is expressed as:



or



$\Delta g_{RbU/Cl_2}$ is an empirical parameter and may be composition dependant, if $\Delta g_{RbU/Cl_2} = 0$ then random mixing occurs, if $\Delta g_{RbU/Cl_2} < 0$, then Equation 8 is displaced to the right with (Rb⁺-Cl⁻-U⁴⁺) pairs becoming predominant.

The Gibbs energy change $\Delta g_{AB/Cl_2}$ associated with the SNN-FNN reaction is given by:

$$\Delta g_{RbU/Cl_2} = \Delta g_{RbU/Cl_2}^0 + \sum_{i \geq 1} g_{RbU/Cl_2}^{i0} x_{RbU/Cl_2}^i + \sum_{j \geq 1} g_{RbU/Cl_2}^{j0} x_{RbU/Cl_2}^j \quad (3.9)$$

Where $\Delta g_{RbU/Cl_2}^0$ and g_{RbU/Cl_2}^{i0} are composition independent coefficients that may vary with temperature. Note that the terms with subscript RbU/Cl_2 and URb/Cl_2 represent the same pairs and can be used interchangeably within the software. x_{RbU/Cl_2}^i is composition dependant function, defined as the fraction to cation-cation pair mole fractions X_{RbRb} , X_{RbU} and X_{UU} :

$$x_{RbU/Cl_2} = \frac{X_{RbRb/Cl_2}}{X_{RbRb/Cl_2} + X_{RbU/Cl_2} + X_{UU/Cl_2}} \quad (3.10)$$

As the composition of RbCl - UCl₄ binary systems changes, the quadruplet approximation model must maintain other parameters to satisfy the conservation of charge whilst simultaneously considering how the FNN and SNN coordination number varies. By assuming the cation SNN coordination number and the charges of cation/anion remains constant, the anion SNN coordination number is fixed in the quadruplet by:

$$\frac{q_{Rb}}{Z_{RbU/Cl_2}^{Rb}} + \frac{q_U}{Z_{RbU/Cl_2}^U} = \frac{q_{Cl}}{Z_{RbU/Cl_2}^{Cl}} + \frac{q_{Cl}}{Z_{RbU/Cl_2}^{Cl}} \quad (3.11)$$

Where q_i are the charges of anions and cations, and Z_{RbU/Cl_2}^i are the SNN coordination number of the respective ion in each quadruplet. For both end members, the quadruplet formations include (U⁴⁺-Cl⁻-U⁴⁺), (Rb⁺-Cl⁻-Rb⁺), (Rb⁺-Cl⁻-U⁴⁺) SNNs. Their excess Gibbs energy expressions are expressed $\Delta g_{RbRb/Cl_2}$, $\Delta g_{RbU/Cl_2}$ and $\Delta g_{UU/Cl_2}$.

The current work introduces a mixture of U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} (with coordination numbers in indices) into the pure liquid UCl₄ as the same complexes and surrogate complexes were identified in Raman spectroscopy studies with ThCl₄ and ACl mixtures (A = Li, Na, K). This permits three different compositions of second nearest neighbour-short range ordering (SNN-SRO). U_v^{4+} is the five-coordinated U⁴⁺, corresponding to the [UCl₅]⁻ “complex-anion”, U_{vi}^{4+} is the six-coordinated U⁴⁺, corresponding to the [UCl₆]²⁻ “complex-anion” and U_{vii}^{4+} is the seven-coordinated U⁴⁺, corresponding to the [UCl₇]³⁻ “complex-anion” (**Fig. 3.4a-c**). Other U complexes have been identified in molten salt mixtures, such as the dimer [U₂Cl₁₄]⁶⁻, which has the same ordering composition as [UCl₇]³⁻. For the sake of simplicity, [U₂Cl₁₄]⁶⁻ has been excluded, but could be included in future work, for example, if deemed necessary to assign it a different transference number to [UCl₇]³⁻ for electro pyroprocessing requirements in the back end to help close the fuel cycle for MSFRs. For the model to maintain mass balance and for conservation of charge, the three different uranium complexes balance with the according Rb⁺ cations as SNNs as shown as in **Fig 3.4a-c**.

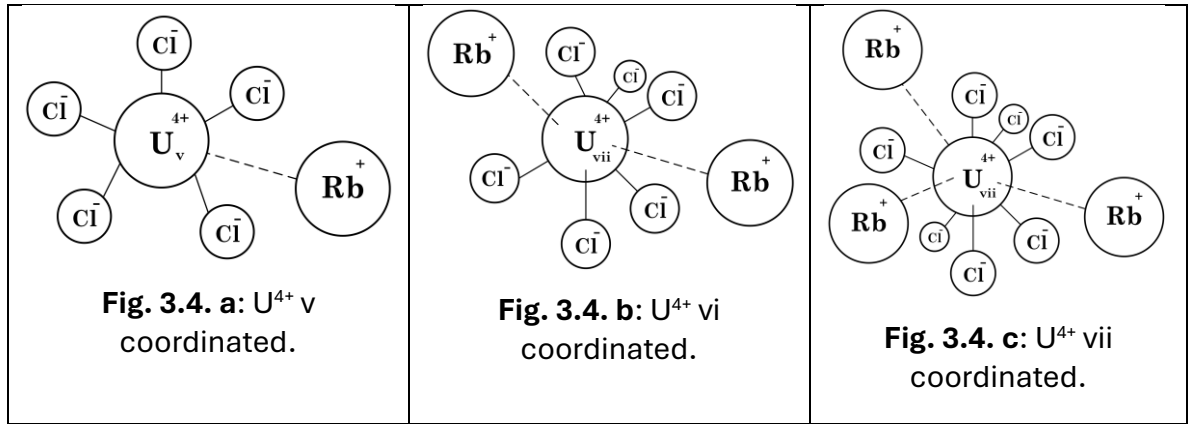


Fig. 3. 4: Visual structural models proposed for the liquid RbCl- UCl_4 molten salt complexes, solid-lines indicating FNN and dashed-lines indicating SNN whilst maintaining overall charge neutrality.

Following this methodology, the following complexes $[UCl_5]$, $[UCl_6]^{2-}$ and $[UCl_7]^{3-}$ have SRO at compositions $X(UCl_4)$ at 0.5, 0.333 and 0.25 respectively. The final results show that this model excluding any dimers can satisfactorily reproduce all experimental phase diagram data and predicted enthalpy of mixing.

As this model incorporates various uranium cations, pure UCl_4 liquid becomes a mixture of U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} cation species and respectively F^- anions. From the Raman spectroscopy data mentioned previously [96] with increasing $ThCl_4$, it was assumed that the U_{vi}^{4+} is the dominant species. Further justification of the dominant species having maximum SRO at the composition of 50 mol% in the RbCl binary salt mixtures, seen by general deep eutectic at $0.44 \geq X(UCl_4) \geq 0.55$. Therefore, to have negligible amounts of U_{vi}^{4+} and U_{vii}^{4+} inside this range, the liquid end-members U_vCl_4 , $U_{vi}Cl_4$ and $U_{vii}Cl_4$ have been destabilised (**Table 3.2**). A positive Gibbs energy contribution has added as shown in **Table 3.3**, to vary the complexes with composition but not with temperature – which may be of interest to future work. The small contribution to the entropy of configuration due to the mixing of the different cationic uranium species does not affect the melting points of UCl_4 .

The resulting molten salt binary system has the Gibbs free energy calculation by the Factsage software by summing the Gibbs free energies of the various quadruplets along with the energy contributed by the configurational entropy resulting from the distribution of the quadruplets on the lattice sites as expressed below:

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$$G = \sum_{i=U_v U_{vi} U_{vii}} \sum_{j=Rb} \sum_{k=Cl} n_{ij/kk} g_{ij/k}^0 - T \Delta S^{config} \quad (3.12)$$

Where $n_{ij/kk}$ is the number of moles of the ij/kk quadruplet, $g_{ij/k}^0$ is the molar Gibbs free energy of the ij/k quadruplet, and ΔS^{config} is the configurational entropy of mixing. A definitive mathematical description of the entropy term is not presently established; however, an appropriate expression was proposed by Pelton *et al* (2000) [60]. The approximation was later improved by Chartrand *et al* (2001) [28] to treat FNN and SNN SRO. $n_{ij/kk}$ is the number of moles of quadruplets, which requires a minimisation of the Gibbs free energy of the molten salt binary solution at a known temperature, pressure and composition – this embodies the equilibrium configuration of both the FNN and SNN. Although the SNN numbers are not used to physically characterise the complexes within the salt solution, they are model parameters allowing them to define the composition of which maximum SRO occurs. This is constrained by charge neutrality, by Eq. 3.13 and following Z numbers used in this model in **Table 3.3**.

Table 3. 3: SNN “coordination numbers” for quadruplets ABXX (with X = Cl) used in the MQMQA for the liquid.

A	B	X	$Z_{AB/XX}^A$	$Z_{AB/XX}^B$	$Z_{AB/XX}^X$	$Z_{AB/XX}^X$
Rb	U_v	Cl	6	6	2.4	2.4
Rb	U_{vi}	Cl	3.6	7.2	2.4	2.4
Rb	U_{vii}	Cl	8.4	2.8	2.4	2.4
U_v	U_{vi}	Cl	6	7.2	1.364	1.364
U_v	U_{vii}	Cl	6	8.4	1.75	1.75
U_{vi}	U_{vii}	Cl	7.2	8.4	1.938	1.938

The modified solution model builds on the composition dependent Gibbs energy exchange Eq. 14 as there are more than two simple cations; Rb^+ and U^{4+} , there are the proposed four; Rb^+ , U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} . Composition variables proposed in Eq. 3.8 are now accordingly proposed as the following:

$$\chi_{RbU_v/Cl_2} = \chi_{RbU_{vi}/Cl_2} = \chi_{RbU_{vii}/Cl_2} = X_{Rb_2/Cl_2} \quad (3.13)$$

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$$\chi_{U_v Rb/Cl_2} = \chi_{U_{vi} Rb/Cl_2} = \chi_{U_{vii} Rb/Cl_2} = X_{(U_v)_2/Cl_2} + X_{(U_{vi})_2/Cl_2} + X_{(U_{vii})_2/Cl_2} + X_{U_v U_{vi}/Cl_2} + X_{U_v U_{vii}/Cl_2} + X_{U_{vi} U_{vii}/Cl_2} \quad (3.14)$$

$$\chi_{U_v U_{vi}/Cl_2} = \chi_{U_v U_{vii}/Cl_2} = \frac{(X_{U_v U_{vi}/Cl_2} + X_{U_v U_{vii}/Cl_2})}{(X_{(U_v)_2/Cl_2} + X_{(U_{vi})_2/Cl_2} + X_{(U_{vii})_2/Cl_2} + X_{U_v U_{vi}/Cl_2} + X_{U_v U_{vii}/Cl_2} + X_{U_{vi} U_{vii}/Cl_2})} \quad (3.15)$$

$$\chi_{U_{vi} U_v/Cl_2} = \chi_{U_{vi} U_{vii}/Cl_2} = \frac{(X_{U_{vi} U_v/Cl_2} + X_{U_{vi} U_{vii}/Cl_2})}{(X_{(U_v)_2/Cl_2} + X_{(U_{vi})_2/Cl_2} + X_{(U_{vii})_2/Cl_2} + X_{U_v U_{vi}/Cl_2} + X_{U_v U_{vii}/Cl_2} + X_{U_{vi} U_{vii}/Cl_2})} \quad (3.16)$$

$$\chi_{U_{vii} U_v/Cl_2} = \chi_{U_{vii} U_{vi}/Cl_2} = \frac{(X_{U_{vii} U_v/Cl_2} + X_{U_{vii} U_{vi}/Cl_2})}{(X_{(U_v)_2/Cl_2} + X_{(U_{vi})_2/Cl_2} + X_{(U_{vii})_2/Cl_2} + X_{U_v U_{vi}/Cl_2} + X_{U_v U_{vii}/Cl_2} + X_{U_{vi} U_{vii}/Cl_2})} \quad (3.17)$$

Eq. 3.12 represents the total Gibbs free energy on the overall system as a given composition and temperature, therefore the expression for the configurational entropy of mixing (ΔS^{conf}) necessitates FNN pair fractions to mitigate convergence between quadruplets and other sets of quadruplets. The parameter ζ is introduced which is defined as the number of quadruplets emanating from a FNN pair, in this case, a $Rb^+ - Cl^-$ or $U^{4+} - Cl^-$ pair. In other molten salt models using the improved MQMQA, authors have varied ζ , normally to account for the reciprocal systems containing significant differences of anionic radii, such as F^- and CO_3^{2-} . In this work, ζ has been kept equal to 2.4, as proposed by Chartrand et al for Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}/F^- , Cl^- reciprocal system.

Lastly, the $\Delta g_{RbU/Cl_2}$ of all the quadruplets were manually optimised without the use of Optisage software to fit the previous and new experimental phase diagram data explored in this work – alongside the anticipated enthalpy of mixing. The $\Delta g_{RbU/Cl_2}$ coefficients are usually expressed as $A + BT$, where A and B are optimised

individually to achieve the possible fit to the data. In this work, as the RbCl-UCl₄ binary system is more complex, exhibiting two different eutectics, rather than a simple singular eutectic found in the NaCl-RbCl system, more coefficients were introduced, A typically being the constant enthalpic term, and the others being entropic that vary with temperature, such as:

$$\Delta g_{RbU/Cl_2} = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E \cdot T^3 \quad (18)$$

3.5 Experimental procedure

The same procedure was used as outlined in Chapter 2, Section 5 to keep data curation consistent.

The reagents used are:

Uranium tetrachloride (UCl₄) anhydrous powder was from International Bio-Analytical Industries (as supplied, 5 g batch, purity 99.99%).

Rubidium chloride (RbCl) powder was from Sigma Aldrich (as supplied, 2 g batch, purity 99.8%).

For TGA-DSC calibration the standards reagents used are given in **Table 3.4** prior DSC fluoride experiments.

As the UCl₄ came dehydrated and packaged within a sealed container flooded with argon. Dr. Sardar also carried out preliminary XRD tests on the UCl₄ from the same supplier and confirmed the sample did not contain water, and so did not require any further purification or dehydration. The RbCl was previously purchased from another supplier – Alfa Aesar, with higher purity 99.975% tested by DSC measurement and multiple peaks alongside a lower melting point indicated that the RbCl was hydrated. This batch was treated by heating to 250°C under strong vacuum (2.8 Torr) in a Schlenk flask, for several hours, then flushed with dry argon at atmospheric pressure momentarily – and this process was repeated for 2 days – yet subsequent DSC testing of the pure sample still indicated partial hydration. Another supplier, Sigma Aldrich, with slightly lower purity (99.8%) was tested and this batch indicated one clear DSC peak from fusion, which was in line with literature values with M.P. of 720°C and enthalpy of fusion with 201 J g⁻¹.



Fig. 3. 5: Sealed sample (below) and reference (above) DSC crucibles on horizontal Hitachi STA72000 sample holders post-experiment displaying minor oxidation on the outer surfaces.

3.6 Results and discussion

3.6.1 Transition temperature measurements of the RbCl-UCl_4 system

As discussed in the previous section, 4 heating cycles and 3 consecutive cooling cycles were programmed into the Hitachi STA-7300 software to carry out one experiment for each separate RbCl-UCl_4 composition. As reported by other authors, such as Sooby et al. (2012) [97], molten salts are prone to exhibit supercooling, giving large variations in onset temperature of DSC peaks and were therefore not used for phase transition data in the phase diagram. The cooling peaks however did produce sharper shoulders and were easier to interpret, thus were used as indication of the number of invariant phase changes rather than the temperature of phase equilibria. The DSC data presented in this work was measured by the onset and offset of the peaks, shown in **Figs. 3.6a & 3.b.**

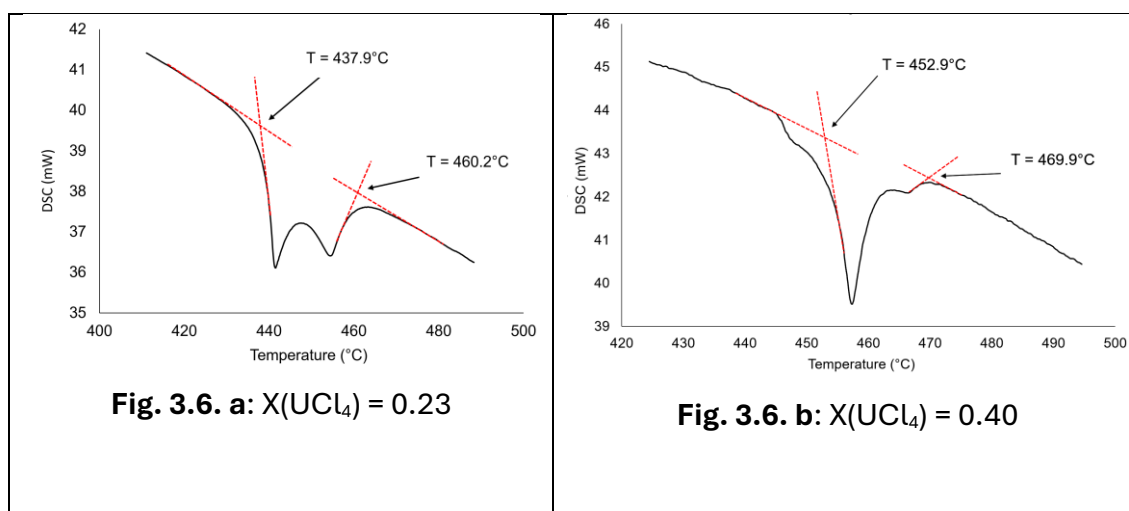


Fig. 3. 6: DSC signal from 2nd heating cycle. Conditions: a at 8°C min^{-1} for composition $X(\text{UCl}_4) = 0.23$; b at $10^\circ\text{C min}^{-1}$ for composition $X(\text{UCl}_4) = 0.40$.

The invariant point data are reported in **Table 3.4** comparing literature data with data gained in this study by extrapolating the DSC signals for onset and offset temperatures. They concern compositions from 0.06 to 0.86 mol of UCl_4 per mol of $(\text{RbCl} + \text{UCl}_4)$ and temperatures from room temperatures to temperature limits expressed in **Fig. 3.7** to prevent crucible failure due to high volatility.

Table 3. 4: Comparison of invariant point data. L for liquid phase.

Invariant Phase Reaction	Type of equilibrium	UCl_4 Mole fraction $X(\text{UCl}_4)$	Temperature $T (^\circ\text{C})$	Reference
$\text{L} \leftrightarrow \text{RbCl} + \text{Rb}_2\text{UCl}_6$	Eutectic	0.21	430	This work
$\text{L} \leftrightarrow \text{Rb}_2\text{UCl}_6$	Congruent melting	0.33	630	Barton <i>et al</i> (1953) [98]
		0.25	519	This work
$\text{L} + \text{Rb}_2\text{UCl}_6 \leftrightarrow \text{RbUCl}_5$	Eutectic	0.40 – 0.50	350	Barton <i>et al</i> (1953) [98]
		0.43	445	This work
$\text{L}' \leftrightarrow \text{UCl}_4 + \text{RbUCl}_5$	Peritectic	0.50	360	Barton <i>et al</i> (1953) [98]
		0.50	450	This work

3.6.2 Phase diagram of the UCl_4 – RbCl system

The phase equilibria temperature data obtained from heating cycles were generally consistent, and some difficult to interpret – indicating more complex chemistry of the actinide tetrachlorides. However, results from cooling cycles showed greater variability due to supercooling which has been commonly observed within the literature, especially with chloride and fluoride salts. Despite this, the cooling cycles yielded more clearly defined and interpretable DSC peaks, which proved valuable in identifying the number and nature of equilibrium points for each composition studied.

No data for the RbCl - UCl_4 binary phase diagram exists to date therefore this is the first attempt at producing it whilst simultaneously completing the thermodynamic optimisation. In the literature, the first mention of phase diagram data was from the ORNL-1649 Quarterly report, *Thermal Analysis of Chloride Systems* by Barton & Boyer (1953) [98]. They mention of preliminary data with indication of the compound Rb_2UCl_6 congruently melting at 630°C and that a eutectic in the 40-50 mol% region that melts approximately at 340°C . It is not clear which techniques were used – but it is suspected that quenching was used – therefore, lower temperatures could be recorded due to supercooling effects.

The second and the last description of the RbCl - UCl_4 binary phase diagram comes in the ORNL-1692 quarterly report, *Thermal Analysis of Chloride Systems* with Wilkerson *et al.* (1954) [99] reporting that UCl_4 systems, particularly the KCl - UCl_4 and RbCl - UCl_4 systems, have shown poorer reproducibility of thermal effects than the UCl_3 systems, and the liquidus for these two systems cannot at the present time be located with certainty in the low-melting- point regions extending from about 40 - 60 mol % UCl_4 . This may be due to UCl_4 volatility, yet not for UCl_3 which has a higher melting point and thermodynamic stability as higher temperatures.

From all DSC experimental data carried out in this work – it was evident that no thermal effects occurred within the 40-60 mol% UCl_4 range at 340°C – but consistent data indicating possible eutectic at 15 – 22 mol% UCl_4 at $\sim 430^\circ\text{C}$, and at $\sim 445^\circ\text{C}$ within 40 – 50 mol% UCl_4 – with less consistent liquidus data.

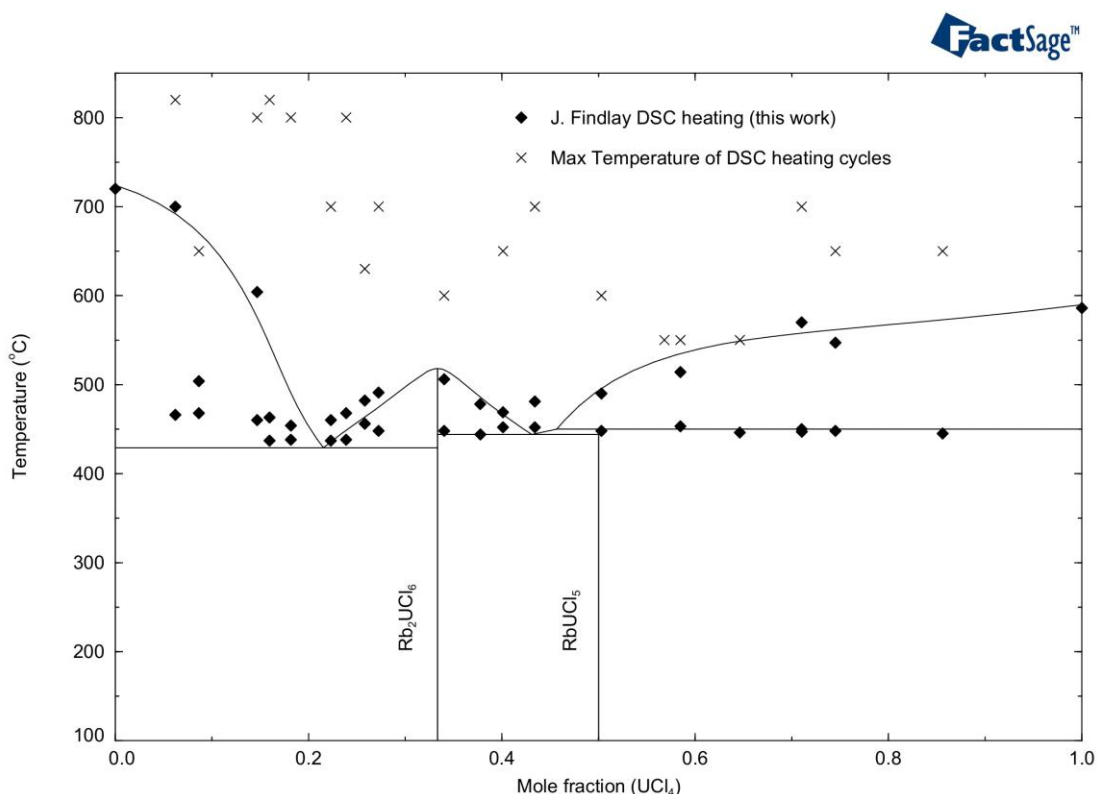


Fig. 3. 7: Comparison of the calculated RbCl-UCl₄ phase diagram with the experimental data points from this work • This work, x Maximum temperature of DSC heating cycles

3.6.3 Enthalpy of mixing

No experimental data currently exists for the enthalpy of mixing in the RbCl – UCl₄ system, therefore an analytical estimate was calculated using all available data from other tetravalent AX-MX₄ systems (where A = Li, Na, K, Rb, Cs and M = U, Th, Zr). UCl₄, ZrCl₄ and ThCl₄ share structural and chemical similarities in terms of morphology, crystallography, phase behaviour, and ionic radii, as does when comparing UF₄, ZrF₄ and ThF₄. This makes these systems useful when comparing phase diagrams, intermediate compounds and enthalpy of mixing.

The enthalpy of mixing data, both experimental and calculated system from different authors for all these systems was used as a proxy for estimation by plotting them as a function of δ_{12} (Equation 3.4) and noticing a general trend. Across various experimental studies on both chloride and fluoride salts, a consistent trend has been observed: as the difference in ionic radii between the two cations increases, the enthalpy of mixing becomes more negative. This trend is particularly evident in

studies involving lanthanide chlorides, and also in MF_4 -based mixtures (where $\text{M} = \text{Zr}, \text{U}$ and Th), where a progressive shift from LiF to NaF , and KF results in increasingly negative mixing enthalpies and that the minima begin to shift from $X(\text{MX}_4)$ 0.5 to $X(\text{MX}_4)$ 0.3-0.4.

In support of this approach, work by Ocadiz-Flores *et al.* (2021) [82] indicated that the enthalpy of mixing for the ACl-ThCl_4 system is more negative than that of the AF-ThF_4 system. As previously mentioned, modelling the first iterations of the liquid applying the same logic as Ocadiz-Flores, introducing more negative enthalpic parameters of the solution resulted in the enthalpies of formation of the solid intermediate compounds were significantly more negative than the values given by Konings *et al.* (2010) [79] to stabilise them at low temperature. Large positive entropic terms introduced in these iterations proved not to be adequate for phase diagram reconstruction – therefore less negative enthalpic parameters were used instead as a means of compromise.

It is important to note that this estimation served primarily as a reference for calibrating the enthalpic parameters in the liquid RbCl-UCl_4 molten salt system. Entropic contributions were subsequently introduced to reproduce key thermodynamic features, such as the liquidus line and eutectic composition, relevant to molten salt reactor applications.

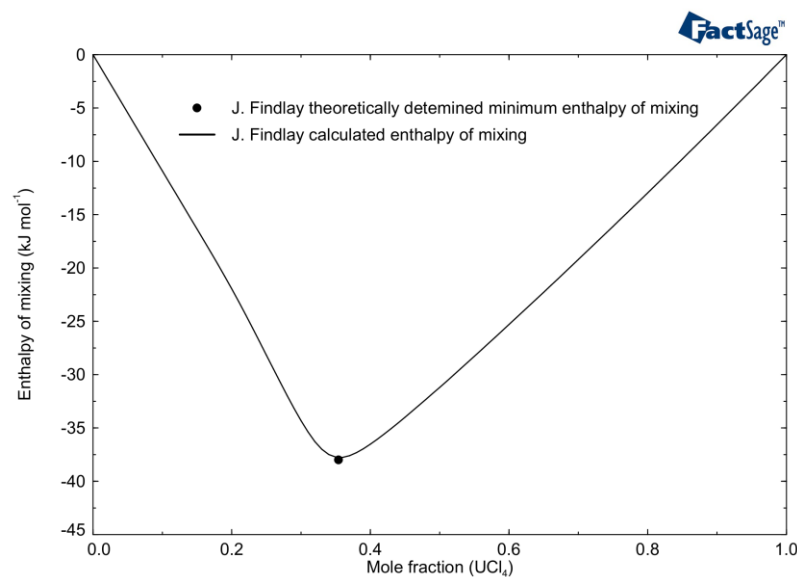


Fig. 3. 8: Calculated enthalpy of mixing of the RbCl-UCl_4 liquid solution

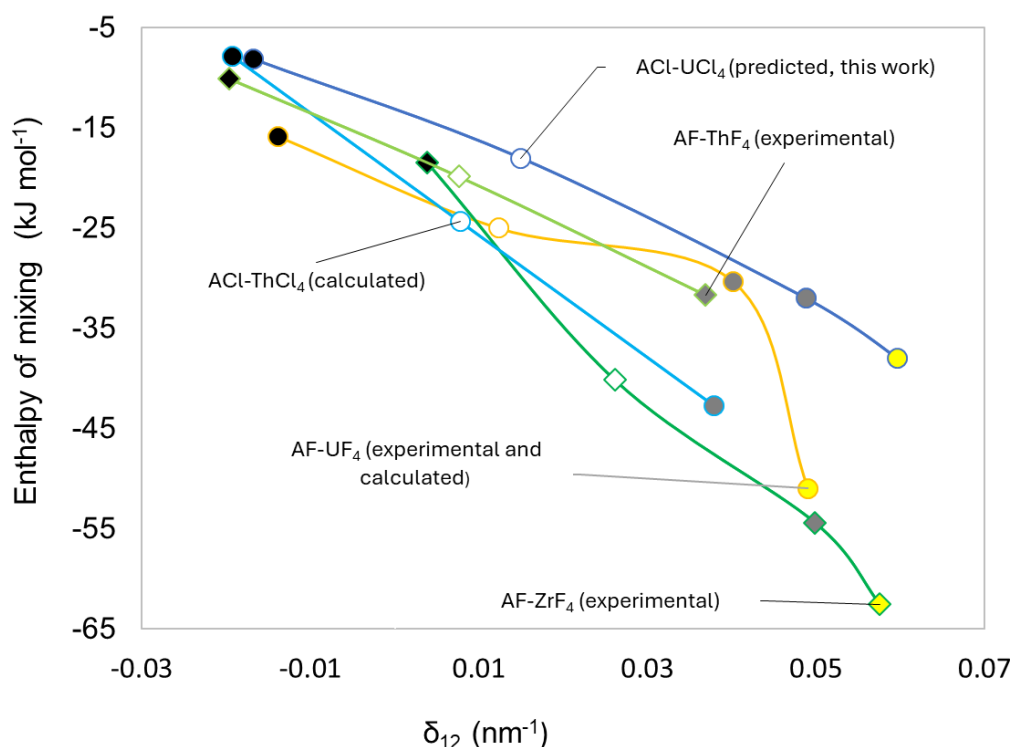


Fig. 3. 9: Experimental and calculated minimum enthalpy of mixing data of MX_4 - AX systems (where $M = \text{Zr, U, Th}$, $\text{Alk} = \text{Li, Na, K, Rb}$ and $X = \text{F, Cl}$) and δ_{12} as defined in Equation 3.4. The black circles represent LiX , white filled circles = NaX , grey = KX and yellow = RbX . As the entire AlkF-ZrF_4 and AlkCl-ThCl_4 systems are produce by Hatem et al (1989) [100] exp. And Ocadiz-Flores et al. (2021) [82] calc. respectively, other separate systems LiF-ThF_4 by Capelli *et al* (2013) [101] exp., NaF-ThF_4 by Schreuder *et al* (2021) [102] exp., KF-UF_4 by Ocadiz-Flores et al. (2020) exp., LiF-UF_4 by Ocadiz-Flores *et al.* (2021) [103] exp., NaF-UF_4 and KF-UF_4 by Schacherl *et al.* (2021) [104] calc., and RbF-UF_4 by Findlay et al. (2026) [65] calc.

All tetrahalide systems mixed with AlkX systems – typically excluding LiX – seem to indicate a non-symmetric enthalpy of mixing, with a local minimum between 30 and 40 mol% of the tetravalent component. With many Raman Spectroscopy studies confirming the presence of various complexes within the melt. This should be of most importance to later models building on the current work and Gibbs energy optimisation using the multi-component complex method – as this can linked

directly to viscosity and density and other physical-chemical properties as shown by Robelin et al. (2007) [31].

3.6.4 Liquid solution and short-range ordering

In this study, the liquid solution is modelled using the modified quasi-chemical model in the quadruplet approximation (MQMQA), which accounts for short-range ordering among both first-nearest neighbours (FNNs) and second-nearest neighbours (SNNs) through the inclusion of quadruplet interactions, as detailed in Section 4. The Gibbs energies of the three selected complexes representing a pure liquid UCl_4 solution were constrained by introducing entropic parameters that maintained constant complex compositions across all temperatures, as described by Eq. 3.19-21, yet allowing the six coordinated uranium chloride complex to be the more dominant species as discussed in more detail in this section.

To ensure thermodynamic consistency, a small correction was determined through manual iteration and uniformly applied to the standard Gibbs energy functions of all complexes. This adjustment was necessary to stabilize the system and bring the complexes into equilibrium with pure UCl_4 . Without this correction, the Gibbs energy values of the uranium–chloride complexes would be excessively negative, resulting in a disproportionate thermodynamic dominance that would destabilize the presence of Rb^+ ions in the melt.

Table 3. 5: Liquid solution parameters, Gibbs free energies g° (J mol^{-1})

$g_{\text{U}_v\text{Cl}_4}^\circ = g_{\text{UCl}_4}^\circ + 30.24207 \cdot (T/K)$	(3.19)
$g_{\text{U}_{vi}\text{Cl}_4}^\circ = g_{\text{UCl}_4}^\circ + 0.24207 \cdot (T/K)$	(3.20)
$g_{\text{U}_{vii}\text{Cl}_4}^\circ = g_{\text{UCl}_4}^\circ + 50.24207 \cdot (T/K)$	(3.21)
$\Delta g_{\text{RbU}_{vii}/\text{Cl}_2} = -26000 - 19.5 \cdot (T/K)$	(3.22)
$\Delta g_{\text{RbU}_{vi}/\text{Cl}_2} = -35000 - 1.2 \cdot (T/K) + \left(2.7 \cdot T (T/K) \cdot \ln \left(\frac{T}{K} \right) \chi_{\text{RbU}_{vi}/\text{Cl}_2} \right) + \left(1.5 \cdot T (T/K) \cdot \ln(T/K) \chi_{\text{U}_{vi}\text{Rb}/\text{Cl}_2} \right)$	(3.23)
$\Delta g_{\text{RbU}_v/\text{Cl}_2} = -37000 + 2.8 \cdot T (T/K) \cdot \ln (T/K) + \left(-10000 + 2.7 \cdot T (T/K) \cdot \ln (T/K) \right) \cdot \chi_{\text{U}_v\text{Rb}/\text{Cl}_2}$	(3.24)

Using these parameters, along with the thermodynamic data for the solid uranium- and rubidium-containing compounds provided in Table 6, the phase diagram shown in **Fig. 3.10** was calculated. The two eutectic points of interest were successfully reproduced, showing strong agreement with both previously reported literature data and the new experimental DSC results presented in this study (see **Fig. 3.10**).

The three standard Gibbs free energy functions of the three uranium complexes in the liquid solutions were set in Eq.'s 3.22-24. This gave maximum SRO at different compositions, for $[\text{UCl}_7]^{3-}$ at $X(\text{UCl}_4) = 0.25$, $[\text{UCl}_6]^{2-}$ at $X(\text{UCl}_4) = 0.33$ and $[\text{UCl}_5]^-$ at $X(\text{UCl}_4) = 0.5$.

The g^0 values shown in Equations 3.19-24 were chosen to let the six-coordinated complex, $[\text{UCl}_6]^{2-}$ dominate in the melt – shown by Raman Spectroscopy experimental data in the ThCl_4 paper by Photiadis *et al* (1999) [96] with proof of existence of the seven coordinated complex, $[\text{UCl}_7]^{3-}$ also existing in the melt but at lower amounts and more in the ACl rich side. In some of the first iterations of the liquid solution, these were the only two complexes that were chosen to be modelled, however, this failed to successfully reproduce the phase diagram whilst simultaneously maintaining the enthalpy of mixing to determined value and minima at the composition of maximum SRO at $X(\text{UCl}_4) = 0.35$.

In another piece of literature by M. V. Smirnov *et al* (1984) [105] the thermodynamic properties of ACl-HfCl_4 mixtures were explored. Presence of $[\text{HfCl}_5]^-$ complexes were confirmed in the mixtures, but also the decomposition of the complexes when vaporisation the melting to produce the pure HfCl_4 vapour. Although not explored in this paper, this will be an important consideration when building the vapour phase in future works contributing to building up molten salt thermodynamic databases for MSFR based on chloride salts. When the $[\text{UCl}_5]^-$ was introduced into the iterations of the model, it was found to successfully reproduce the phase diagram whilst maintaining the enthalpy of mixing at the determined values and the minima at the right compositions. As seen from Table 3.5, many positive entropic parameters were used, aligning with the idea that for this specific binary mixture, RbCl-UCl_4 has been found to be quite volatile, whilst most likely possessing rather negative enthalpic contributions.

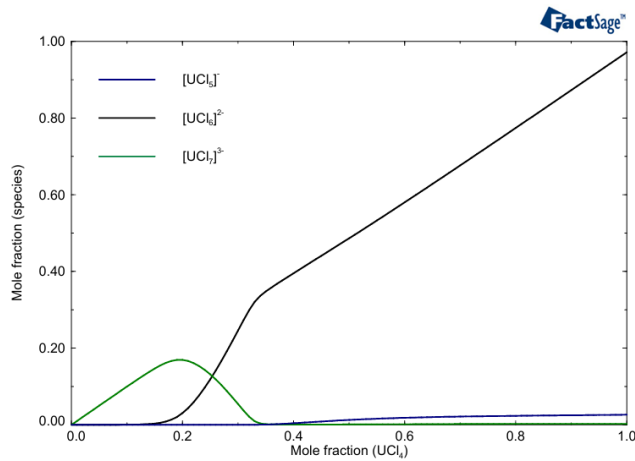


Fig. 3. 10: Mole fraction of uranium complexes in the RbCl-UCl₄ system calculated in this work, T = 500°C.

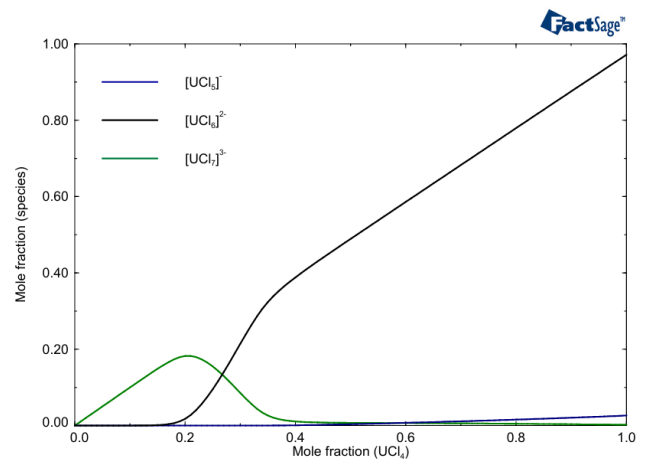


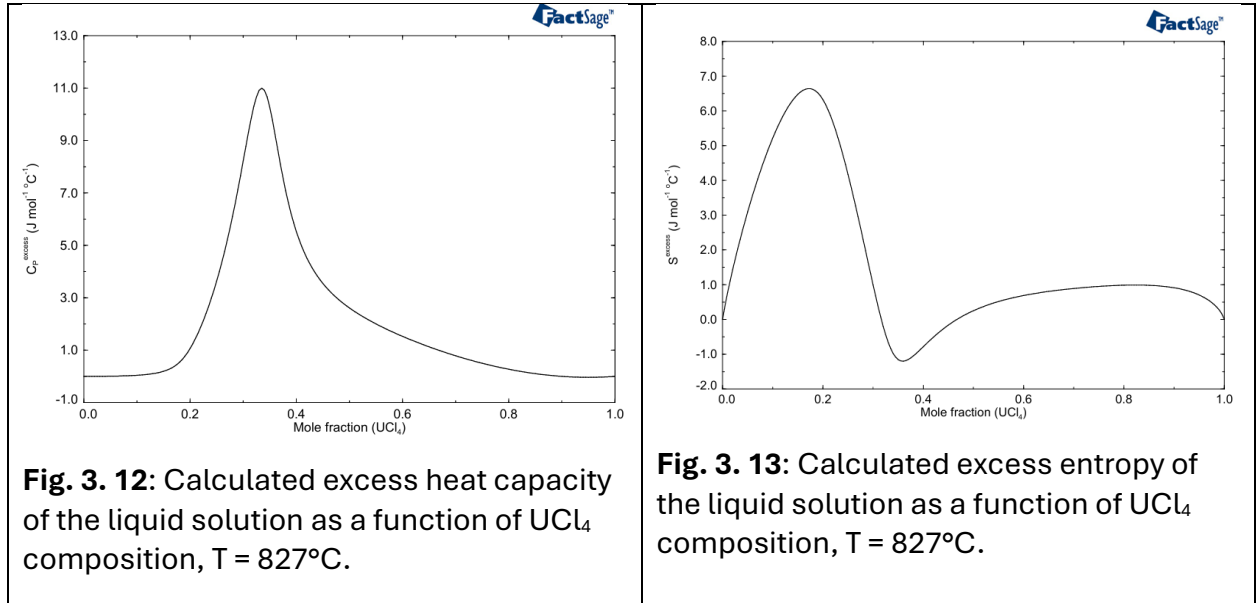
Fig. 3. 11: Mole fraction of uranium complexes in the RbCl-UCl₄ system calculated in this work, T = 827°C.

3.6.5 Excess properties

Determining the excess thermodynamic properties of molten salt mixtures is a key focus of this work. Experimental measurements of heat capacity for such systems are limited, with only a few studies addressing the variations in thermophysical properties. In previous work, Roger et al. (1982) [72] experimentally measured

notable deviations in the molten FLiNaK (46.5 mol% LiF, 11.5 mol% NaF, 42.0 mol% KF) system, from predictions based on the Neumann–Kopp rule, a trend also observed in recent C_p measurements of the molten FLiBe (66.7 mol% LiF, 33.3 mol% BeF₂) system by Lichtenstein (2020) [73].

As shown in Table 6, numerous entropic parameters were required to accurately reproduce the phase diagram and the three eutectic points of the system. This modelling effort also involved simultaneous adjustment of the standard enthalpy of formation and standard entropy for two solid intermediate compounds. In contrast to the LiCl-RbCl phase diagram, which features a single eutectic and one intermediate solid compound, the RbCl-UCl₄ system presents greater complexity due the presence of two eutectics and a known high vapour pressure Salyulev (2022)



[106]. This necessitates the inclusion of higher-order interactions and additional thermodynamic parameters.

Ocadiz-Flores *et al.* (2021) [103] successfully modelled the LiF-UF_4 binary using both molecular dynamics (MD) simulations and the CALPHAD method, showing that the excess properties remained relatively constant across compositions. Here, the calculated excess molar heat capacity and molar entropy of the RbCl-UCl_4 liquid solution at 827°C . These data are plotted as functions of UCl_4 composition in **Figs. 3.12 & 3.13**.

A plausible explanation for these observations lies in the differences in ionic radii given by R. Shannon [107]. The ionic radius of U^{4+} in six-fold coordination (not to be confused with FNN or SNN coordination numbers) is approximately $0.89 \text{ \AA}$, while that of Li^+ (also six-coordinated) is $0.76 \text{ \AA}$. In contrast, Rb^+ has a significantly larger six-coordinated ionic radius of $1.52 \text{ \AA}$, exactly double that of Li^+ . This substantial disparity in ionic size between U^{4+} and Rb^+ could account for the more pronounced deviations in excess thermodynamic properties. A larger ionic radius mismatch tends to introduce greater structural disorder into the melt, which increases vibrational freedom. This, in turn, leads to a rise in heat capacity (C_p) and enhances the overall thermodynamic contributions, causing the system to deviate further from ideal behaviour.

Finally, the heat capacity and entropy of the liquid solutions were calculated as functions of UCl_4 molar fraction at 817 °C (see **Figs. 3.13a&b**). These results show clear deviations from ideal, consistent with the effects of the interaction parameters discussed above.

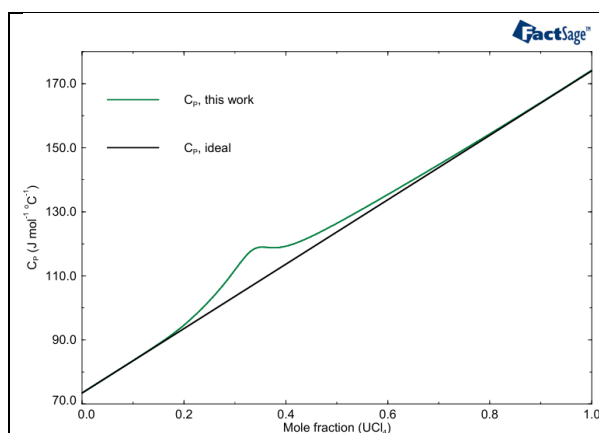


Fig. 3. 14: Calculated heat capacity of the liquid solution as a function of UCl_4 composition, $T = 827^\circ\text{C}$.

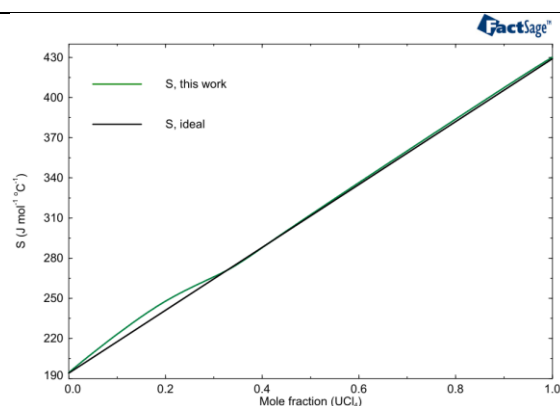


Fig. 3. 15: Calculated entropy of the liquid solution as a function of UCl_4 composition, $T = 827^\circ\text{C}$.

3.6.6 Activity of UCl_4 in liquid phase and reported experimental fugacity

Of particular interest, is the calculation of UCl_4 activity in the liquid phase when comparing to that of some of the very limited experimental data of the RbCl-UCl_4 system that does exist, which quite recently, Salyulev et al. (2022) [106] explore UCl_4 activity in the gaseous phase as shown in **Fig. 3.15**. In Salyulev's other recent work (2021) [108], measuring UCl_4 volatilities in NaCl and KCl mixtures, and measuring UCl_4 volatilities in equimolar NaCl-KCl mixtures, the fugacity of UCl_4 in the vapour phase is notably lower than in the RbCl binary mixture, demonstrated in **Fig. 3.16**. A probable explanation for this is that intermediate compounds, Rb_2UCl_6 , RbUCl_5 and $[\text{UCl}_5]^-$ may have far less stability than A_2UCl_6 and AUCl_5 compounds (where $\text{A} = \text{Na}$ or K). Whereas $[\text{UCl}_7]^{3-}$, has more stability – inhibiting the formation of UCl_4 within the melt – in general agreement with the Salyulev's findings in the gas phase,

Less stability of Rb_2UCl_6 , RbUCl_5 and $[\text{UCl}_5]^-$ would result in increases in the activity of UCl_4 in the liquid phase – which aligns with the results of the model presented here, highlighted by **Fig. 3.16**. From **Fig. 3.17**, we see lower concentration of UCl_4 in the gas phase with increasing UCl_4 content in the liquid phase in the binary NaCl and KCl mixtures. This is hypothesized to be vaporisation of A_2UCl_6 , AUCl_5 and $[\text{ACl}_5]^-$, also indicating greater stability of these species than their Rb containing counterparts.

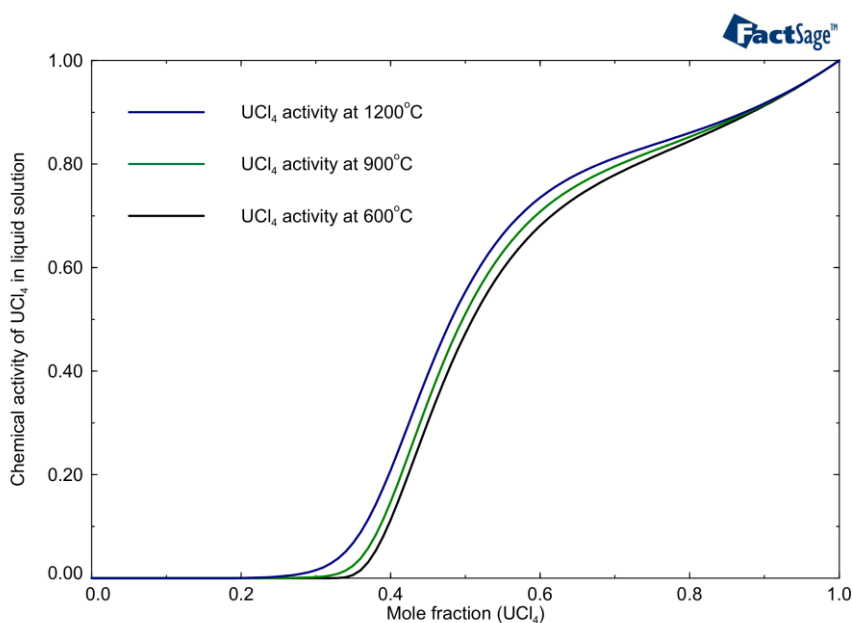


Fig. 3. 16: Calculated activity of UCl_4 in the liquid solution as a function of UCl_4 composition in RbCl , $T = 600^\circ\text{C}$, 900°C and 1200°C

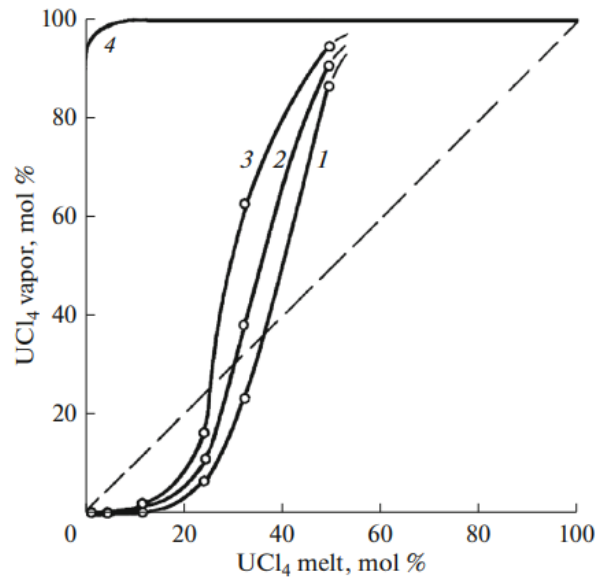


Fig. 3. 17: Experimental fugacity of UCl_4 of the liquid solution as a function of UCl_4 composition in RbCl , $T = 700^\circ\text{C}$ (1), 800°C (2) and 900°C (3), with permission from Elsevier, from Salyulev (2022) [106].

3.6.7 Redox control and corrosion mitigation

In the Molten Salt Reactor Experiment (MSRE), researchers at Oak Ridge National Laboratory (ORNL) recognized that controlling the redox potential of the fuel salt was critical in mitigating corrosion of structural alloys. As a result, advanced high-nickel alloys such as Hastelloy-N were concurrently developed at ORNL to address the corrosion challenges observed with conventional stainless steels. Certain alloying elements in stainless steels, while contributing to their corrosion resistance, were found to dissolve and preferentially leach from surface layers, forming a variety of fluoride species within the molten salt environment. Among these, chromium (Cr), a key component responsible for forming the protective Cr_2O_3 layer, was detected in elevated concentrations in the fuel salt and other salt-loop systems. Surface analysis of the affected alloys confirmed chromium depletion near the exposed surfaces. To further mitigate corrosion, ORNL researchers also optimized the redox potential of the fuel salt (65.0 mol% LiF – 29.1 mol% BeF_2 – 5.0

mol% $\text{ZrF}_4 - 0.4 \text{ mol\% } \text{UF}_4$) by introducing small amounts of UF_3 , rendering the salt more reducing, an approach that proved to be effective.

In chloride-based systems, this is lesser known no chloride based MSR system has operated – only lab scale experiments. Authors Fredrickson et al (2018) [78] explore the importance of redox control of uranium chloride-based salt system by altering the ratio of $\text{UCl}_4/\text{UCl}_3$, yet do not discuss how the redox potential can significantly alter by simple addition of base salts such as AlkCl (where $\text{Alk} = \text{Li, Na, K, Rb}$). In this work, the newly modelled RbCl-UCl_4 (57 mol% - 43 mol%), where the composition of the second eutectic's chloride potential is plotted against other various salts including alloy corrosion product in **Fig. 3.18**:

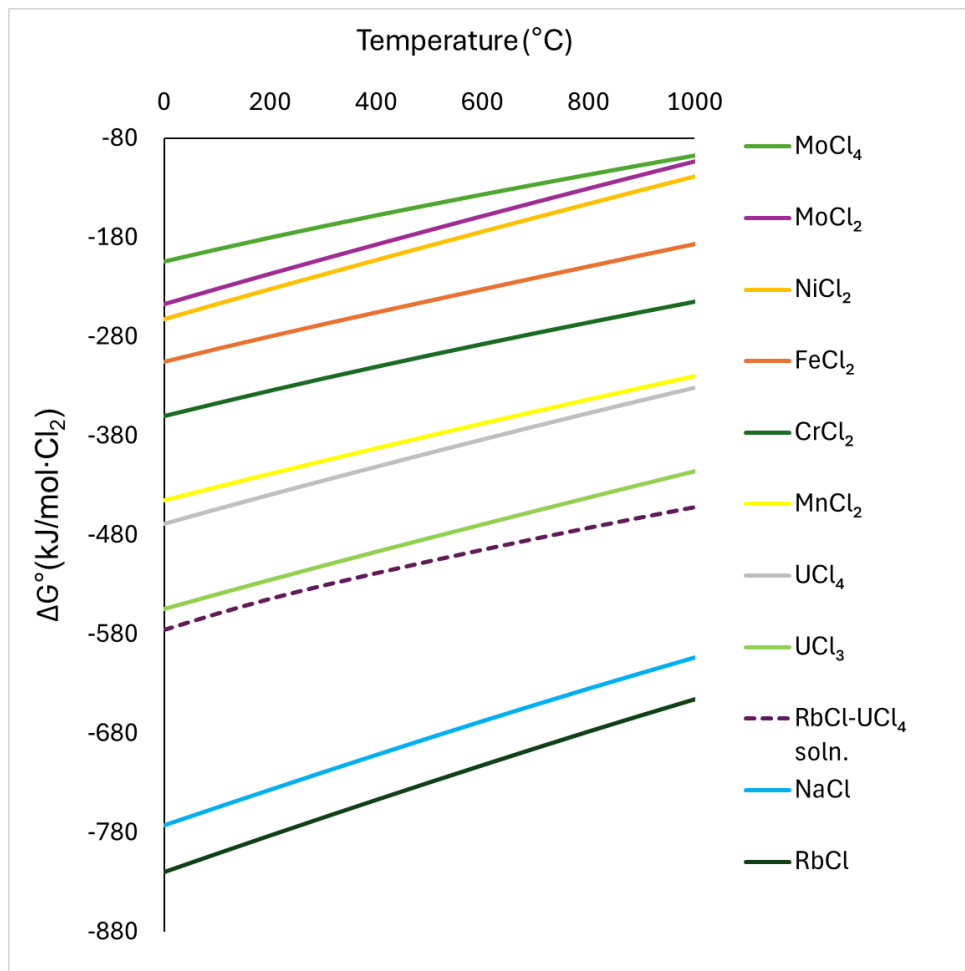


Fig 3. 18: Standard Gibbs free energy of formation per mole of Cl_2 for salt components, corrosion products and molten salt solution ($\text{RbCl-UCl}_4 \text{ soln.}$) of the binary molten salt modelled in this work at composition $X(\text{UCl}_4) = 0.43$. Other data from Gurvich *et al* (1994) [68].

In **Fig. 3.18**, the RbCl-UCl₄ solution, comprising 57 mol% RbCl and 43 mol% UCl₄, corresponding to the composition at the lowest eutectic temperature has been used to evaluate its redox potential in comparison to other chloride salt systems. Notably, UCl₃, which is often hypothesized to exist in small quantities within UCl₄ containing fuel salts to maintain a slightly reducing environment, exhibits a less reducing character than the RbCl-UCl₄ eutectic mixture. This observation provides useful insight into controlling salt thermochemistry: the addition of UCl₃ can potentially make the salt overly reducing. However, since no graphite moderator will be present in the system of a MSFR, the formation of uranium carbides, a known issue in strongly reducing fluoride salt systems in contact with graphite, will not be a concern.

3.6.8 Fuel composition change during operation

The RbCl-UCl₄ system, has been shown to demonstrate rather larger vapour pressure than other binary chloride systems. Nevertheless, benefits include two eutectics at low temperatures and hardening the neutron spectrum within an MSFR core using RbCl as the heavier atomic weighted carrier salt than LiCl, NaCl and KCl.

CsCl, being heavier than Cs is monoisotopic (¹³³Cs) but its neutron absorption cross section is too large (2.5 + 26.5 b, yielding a safety relevant nuclide ¹³⁴Cs) to be used as salt carrier in the fuel. This is not the case of Rb which occurs as (⁸⁵Rb and ⁸⁷Rb) but with small neutron absorption cross sections (0.06 + 0.45 b and 0.10 b, yielding no safety relevant nuclides). In addition to optimises the neutron economy, ³⁷Cl can be separated from ³⁵Cl and used as suggested by and Degueldre & Merk (2023) [87].

In addition to advantages of heavier salts and low eutectic temperatures, the second eutectic at X(UCl₄) = 0.40-0.45 allows for high uranium loading in the fuel - expanding the possibilities of smaller and more compact MSFR cores for applications including, but also outside electricity production in conventional thermal power plants.

UCl_3 is widely acknowledged to be a component in the beginning of life of a MSFR fuel, but as the fission reaction is an oxidative process, yielding UCl_{3+x} , this will result in some production and potential evolution of UCl_4 . This requires accurate analytical measurement on the fuel such as suggested in Degueldre (2017) [109].

With the properties of the fresh fuel now characterized, the evolution of its properties over the course of its operational lifetime can be predicted with greater accuracy.

3.7 Conclusion

The RbCl-UCl_4 system, emerging as a potential fuel for molten salt fast reactor (MSFR), has been experimentally explored and thoroughly analysed in this study for the first time with a focus on its thermodynamic behaviour.

Drawing comparisons with the structurally analogous tetravalent – alkali halide systems, this investigation represents the novel comprehensive modelling of the liquid phase and the calculation of thermodynamic properties for the intermediate solid compounds, i.e. Rb_2UCl_6 and RbUCl_5 complexes, within the RbCl-UCl_4 binary system. These complexes play an important role in the retention of the UCl_4 in the condensed phase retarding its evolution in the gaseous phase.

The study underscores the importance of precise and reliable methodologies for determining thermodynamic properties in systems where experimental data are limited or unavailable. By optimising DSC through using low-mass crucibles, enhancing thermal sensitivity and by expanding the Gibbs free energy functions of uranium-based multi-coordinated complexes within the liquid phase, this work demonstrates a pathway toward accurate thermodynamic modelling with minimal sample requirements, thereby reducing material waste.

As the field of molten salt nuclear technology continues to evolve, the insights gained from this investigation provide a critical foundation for future research into uranium and other actinide-based salt systems, supporting the development of advanced fuel cycles and the next-generation of MSR technologies.

Chapter 4: Experimental thermodynamic modelling study of RbF-CeF₃ system and its application to the RbF-PuF₃ system

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Joshua Findlay¹, David Cheneler¹, Claude Degueldre¹

¹School of Engineering, Lancaster University, Lancaster LA1 4YW UK

4.1 Abstract

The thermodynamic characterisation of the RbF-PuF₃ system was undertaken using CeF₃ as a non-radioactive surrogate for PuF₃, a promising candidate fuel component for Molten Salt Reactors (MSRs). The UK's existing plutonium stockpile, if converted to PuF₃, represents a viable option for molten salt reactor fuels. Incorporating PuF₃ into multicomponent systems may optimise both thermophysical and neutronic properties, making the binary RbF-PuF₃ system a key foundation for more complex fuel salt compositions. Novel DSC data from the RbF-CeF₃ binary, combined with literature sources, enabled a systematic description of phase equilibria across different compositions and temperatures. Particular emphasis was placed on compound purity, phase coexistence, and the use of lightweight custom-designed crucibles, which proved essential for reliable phase diagram reconstruction. In the absence of complete experimental data for intermediate compounds, their thermodynamic properties were estimated using the Neumann–Kopp relation and the CALPHAD method. The liquid phase was described using the Modified Quasichemical Model in the Quadruplet Approximation (MQMQA), applied here for the first time to include liquid complexes of the type [MF₆]³⁻ (M = Ce, Pu). Raman spectroscopy has independently confirmed the presence of these species for M = La and Ce, revealing specific short-range ordering at X(MF₃) = 0.33. This structural information serves as an important reference for the reliable optimisation of more complex RbF-MF₃ systems in future thermodynamic modelling. CeF₃ was selected over LaF₃ in this study due to its closer similarity to PuF₃ in melting point, enthalpy

Chapter 4: Experimental thermodynamic modelling study of the RbF-CeF₃ system and its application to the RbF-PuF₃ system

of fusion, and ionic radius. Its use revealed eutectics at lower temperatures and higher actinide solubility than comparable AlkF-MF₃ (Alk = Li, Na; M = Ce, Pu) systems. Finally, Rb_mM_nF_{3n+m} solid complexes were shown to strongly affect phase behaviour and eutectics, offering greater thermodynamic stability relative to single-eutectic systems such as LiF-PuF₃ and NaF-PuF₃, albeit with slightly higher melting points. The optimised RbF-PuF₃ liquid solution was further assessed with an Ellingham diagram to evaluate redox potentials and possible corrosion resistance improvements.

Keywords: RbF-CeF₃ system; RbF-PuF₃ system; Differential Scanning Calorimetry; Phase diagram; Heat capacity; Molten salt reactor fuel

Corresponding author: j.findlay1@lancaster.ac.uk

4.2 Introduction

Molten Salt Reactors (MSRs) are among the most promising candidates for advanced nuclear systems, owing to their potential for inherent safety, efficient fuel utilisation, and reduced long-lived waste [12]. Their operation relies on liquid fluoride salts serving simultaneously as fuel and coolant, which introduces unique challenges for understanding and controlling thermochemical and thermophysical behaviour under reactor-relevant conditions as reported by Merle-Lucotte et al. (2008) [110]. Reliable thermodynamic data are essential to predict phase equilibria, solubility, and chemical stability as the salt composition evolves during fission and actinide transmutation.

While most prior research has focused on Li- and Na-based fluoride systems, data for RbF mixtures remain limited. Chloride-based salt systems are also viable for MSR fuels; however, the lower atomic mass of the fluoride ion, relative to chloride, improves neutron moderation and could reduce the moderator requirement within the core. In addition, fluorine does not present the same isotopic concerns as chlorine, where neutron capture by ³⁵Cl produces long-lived ³⁶Cl, necessitating

Chapter 4: Experimental thermodynamic modelling study of the RbF-CeF₃ system and its application to the RbF-PuF₃ system

isotopic enrichment. RbF offers potential advantages, including low neutron absorption cross-sections for its two stable isotopes (⁸⁵Rb and ⁸⁷Rb) [111] and altered solubility behaviour for certain fission products such as caesium and iodine [13]. RbF in a solution with actinide salts such as PuF₃ or UF₄, can significantly change thermodynamic and physio-chemical characteristics, which make RbF an interesting alternative carrier salt for further research for actinide-containing molten salts. RbF may be more suitable as a carrier salt in a molten salt fast reactor configuration due to its relatively high mass number. However, with an appropriate reactor geometry and sufficient moderator material, such as graphite, adequate neutron moderation can still be achieved while preserving the distinct physical and thermodynamic properties of RbF. Fluoride salts used in molten salt reactors are broadly comparable to chloride salts; however, although chlorides could possibly be employed in thermal-spectrum MSRs with sufficient moderation, they are generally less suited to such operation. Fluoride salts are typically preferred for thermal-spectrum systems, as the lower atomic mass of the fluoride ion, relative to chloride, enhances neutron moderation efficiency when combined with a suitable moderator such as graphite.

Direct experimental work on Pu systems remains challenging due to radiological constraints. Consequently, Ce is frequently employed as a chemical surrogate for trivalent Pu. As reported by Fortner et al. (1999) [112], CeF₃ closely mirrors PuF₃ in its crystal structure, ionic radius, and bonding characteristics, making it an effective analogue for thermodynamic and phase equilibrium studies, as validated by Ponomarev et al. (2012) [113]. Binary systems containing CeF₃ with alkali metal fluorides have been shown to exhibit phase diagram features and compound formation behaviour analogous to those of PuF₃-based systems.

The RbF-CeF₃ binary system has therefore been selected as an experimental analogue for the RbF-PuF₃ system. Experimental determination of its phase equilibria and thermal properties provides a foundation for the development and optimisation of thermodynamic models capable of describing both systems. This is particularly relevant for molten salt mixtures in which strong ionic interactions cause the solution properties to deviate significantly from ideal behaviour; in such

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systems, complex ion formation and short-range ordering (SRO) can occur in the liquid phase. Traditional regular-solution approaches are insufficient to capture these effects, requiring more advanced formalisms such as the Modified Quasi-Chemical Model with Quadruplet Approximation (MQMQA).

In this work, a combined experimental and computational investigation of the RbF-CeF₃ and RbF-PuF₃ systems is presented. Differential Scanning Calorimetry (DSC) was used to determine key phase transition temperatures for the RbF-CeF₃ system, which served as the experimental foundation for subsequent thermodynamic optimisation using the MQMQA implemented in FactSage Version 8.3 software. The model incorporates the formation of complex ionic species [MF₆]³⁻ (M = Ce, Pu), supported by spectroscopic evidence from prior studies on alkali fluoride systems by R. Cui et al. (2021) [114]. The resulting description provides a physically grounded representation of short-range ordering and non-ideal interactions within the liquid phase. Since MSR fuels will not contain ²³⁹PuF₃ at concentrations exceeding 50 mol% for excessive reactivity issues, it is reasonable at this stage to focus on isolated [MF₆]³⁻ species. Although [PuF₆]³⁻ has not yet been experimentally verified due to a lack of available data, its incorporation is justified through the established surrogate behaviour of Ce for Pu. Certain molten salt solutions have been shown not to exhibit complete random mixing; instead, through Raman Spectroscopy and e.m.f. investigation have found the ions form clusters with short-range ordering (SRO) at specific compositions ([40], [115]), an effect accounted for by this modelling approach. This method, applied to binary systems, provides a foundation for constructing higher-order systems (ternary, quaternary etc.) to maintain robustness and accuracy in thermodynamic predictions.

The optimised RbF-CeF₃ model was subsequently extended to the RbF-PuF₃ system using established analogue behaviour and available thermodynamic data. Together, these results contribute to a more comprehensive understanding of actinide fluoride behaviour in molten salt systems and support ongoing efforts to establish robust databases for advanced reactor applications. The use of the FactSage software enables the calculation of redox potentials for any composition within the optimised molten salt solution, thereby providing deeper insight into its

corrosiveness. In the present work, particular attention is given to the analysis of the two eutectic compositions identified within these systems.

4.3 Background

4.3.1 Phase diagram insights melting phenomena in eutectics for MSRs

The study of phase diagrams and the identification of key points such as liquidus, solidus, eutectic, and peritectic are crucial for the successful operation of Molten Salt Reactors (MSRs). The selection of fuel components and their proportions must meet several criteria, including a melting point compatible with the minimum operating temperature, sufficient density to sustain and control the fission rate, low viscosity for efficient fluid flow, appropriate heat capacity for vessel design, optimal neutronics, and compliance with maximum allowable enrichment for the actinide salt composition. LiF-MF₃ and NaF-MF₃ (M = Ce, U, Pu,) have attractive simple phase diagram with single eutectic temperatures, yet compositionally, the eutectics remain in the alkali metal fluoride rich side at X(MF₃) = 0.2 and 0.3 respectively [116], [117]. Exploring heavier alkali metal fluoride salt binaries, such as KF-MF₃ and CsF-MF₃ not yet investigated experimentally, may produce a second eutectic at higher MF₃ content like the RbF-CeF₃ system shown in this work, but CsF is discarded due to unfavourable neutronics. While further experimental validation is necessary, the incorporation of KF and RbF components to increase the fissile MF₃ (M = U, Pu) concentration within the fuel salt has the potential to markedly improve neutron economy and burnup. Such enhancements could facilitate the development of more compact MSR designs, with consequential reductions in capital expenditure.

Accurate knowledge of the phase diagram is essential for identifying all stable solid compounds within the system. Even during planned shutdowns of an MSR, the solidification of known stable intermediate phases can be reliably predicted through thermodynamic optimisation. Understanding their stability, density, and crystal structure is critical for regulatory assurance, ensuring that no risk of re-criticality arises under such conditions. If cooling causes the temperature to drop

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below the liquidus point in the RbF rich-side, RbF will begin to precipitate from the solution. This process enriches the remaining liquid in PuF₃, which can accelerate the fission rate and increase heat generation. Although the exact mechanisms of solid precipitation from the molten salt are not fully understood, such behaviour could act as a self-regulating process, where the temperature rise re-melts the solidified RbF or, it could be problematic, where RbF remains solidified either on cooler heat exchanger surfaces, further limiting heat removal for power production or floating due to its lower density relative to the bulk melt within the MSR.

Conversely, if the fuel is richer in PuF₃, the actinide salt would precipitate first upon cooling below the liquidus. This could lead to several outcomes, such as deposition on the vessel walls or settling of precipitates at the vessel bottom, depending on the density difference between the solid actinide salt and the molten solution. Such settling could form hotspots, while the depleted fuel salt, with lower actinide concentration, would experience a reduced fission rate, further cooling the system and risking shutdown due to solidification. It is also hypothesised that these hotspots could re-melt PuF₃ precipitates, maintaining a self-regulating reactivity.

Similarly, understanding the chemical activity of each salt component is important. While molten salts have very low vapor pressures, vapor deposition in headspaces is still observed in industrial applications, such as concentrated solar plants using molten nitrate salts [118]. Therefore, determining excess partial Gibbs energies helps better predict vapor deposition during processes like helium purging, fuel processing, or extraction of valuable fission products.

While the gaseous phase is not addressed in the present study, it is a reasonable and methodical approach to prioritise the characterisation of the liquid and solid phases first. These phases form the foundation for building a comprehensive thermodynamic database, which can then support the evaluation and comparison of alternative fuel salt candidates. Subsequent analysis of the gas phase can be conducted once suitable systems have been identified for further investigation.

4.3.2 Prior phase diagram investigations

Limited research has been conducted on RbF-based actinide fuel salt systems, with most phase diagram studies dating back several decades to work carried out at Oak Ridge National Laboratory (ORNL) during the Aircraft Reactor and Molten Salt Reactor Experiment (MSRE) programs. To date, two studies have relevance in this work, RbF-CeF₃ system was predicted by Fedorov et al. (1999) [119] and the RbF-PuF₃ phase diagram was predicted and thermodynamically evaluated using RbF-LaF₃ as a surrogate system by O. Beneš et al. (2008) [120]. Previous thermodynamic modelling by Konings [121] utilised a dataset derived from an internal report by the Institute for Transuranic Elements (ITU), which remains publicly inaccessible. Notably, this dataset reports a standard molar entropy for liquid PuF₃ that is lower than that of its solid phase, an outcome that contradicts fundamental thermodynamic expectations, as the entropy of a liquid should exceed that of the corresponding solid. Due to the inaccessibility of the original source and the apparent inconsistency of these values, the reliability of this data warrants critical evaluation. Accordingly, this study adopts the standard thermodynamic data for pure PuF₃ solid and liquid phases from Gurvich [68]. Furthermore, LaF₃ employed as a surrogate for PuF₃ in the previous modelling effort, may not be as suitable as CeF₃, owing to less comparable physicochemical properties as outlined in Table 1. A similar evaluation for LaF₃ is not possible, as the data is sourced from the same inaccessible report, leaving it unclear whether a comparable inconsistency in standard entropy exists.

Table 4. 1: Comparison of ionic radii, melting temperature and enthalpy of fusion of LaF₃ and CeF₃ as surrogate compounds for PuF₃

Compound	Cation ionic radii	Space group	T _M (°C)	ΔH _{fus} (J mol ⁻¹)	Ref.
LaF ₃	1.032	P $\bar{3}$ c1	1493	50208	Barin [44]
CeF ₃	1.01	P $\bar{3}$ c1	1437	55467	Barin [44]
PuF ₃	1.00	P $\bar{3}$ c1	1426	54392	Gurvich [68]

O. Beneš et al. (2008) [120], using LaF₃ as a surrogate, predicted two eutectics in the RbF-PuF₃ system at X(PuF₃) = 0.214 at 506°C and 0.262 at 526°C. P. Fedorov

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(1999) [119], using available thermodynamic and crystallographic data from various RbCe_xF_y compounds, predicted two eutectics in the RbF-CeF₃ system at X(CeF₃) = 0.14 at 625°C and 0.33 at 690°C.

As more experimental data emerges, it becomes more evident that Ce containing salt, common both to fluorides and chloride binary systems is the most suitable Pu surrogate of the lanthanide series. The historical experimental work carried out Barton et al. (1960) [122] comparing the NaF-PuF₃ and NaF-CeF₃ phase equilibria diagrams support this, the eutectic temperature only differentiating by 1°C and shifted by a few mol% to the right towards PuF₃/CeF₃ rich side.

As demonstrated by this work, the study published by Fedorov (1999) demonstrates the closest phase diagram data than other prediction made by Beneš et al. (2008) for RbF-PuF₃. The estimated phase diagrams of the RbF-PuF₃ system and RbF-CeF₃ system are comparable however both offer a first eutectic followed by a second in both cases.

4.4 Thermodynamic data and crystal structures for pure compounds

4.4.1 Crystallographic data

The crystallographic data of compounds are essential for understanding their structural and physical properties. These data provide insights into the atomic arrangement, space groups, and lattice parameters, which are essential for phase diagram assessments. In this study, the intermediate compounds in the RbF-CeF₃ system each exhibit distinct crystal structures. It is anticipated that the RbF-PuF₃ system will behave similarly. However, documenting these structures remains important, as future development of higher-order systems incorporating the RbF-MF₃ (M=Ce, Pu) binaries may result in intermediate compounds with shared crystal structures. In such cases, depending on the composition and temperature, the presence of structurally compatible phases could permit interstitial cation

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substitution within a common sublattice, rather than the formation of multiple separate solid phases.

In this study, the six involved compounds are reported in literature, two end member compounds (RbF and CeF₃) and four intermediate compounds (RbCe₂F₇, RbCeF₄, Rb₂CeF₅ and Rb₃CeF₆). For the end member compounds RbF and CeF₃, the data are easily available at room temperature.

Table 4. 2: Summary of crystallographic data of RbF-CeF₃ intermediate compounds

Fluoride	RbF mol%	<i>M</i> g mol ⁻¹	Space group	ρ g cm ⁻³	Ref
RbF	100.00	104.466	Fm $\bar{3}$ m* Pm $\bar{3}$ m	3.557 4.53	[123]
Rb ₃ CeF ₆	75.00	510.53	<i>cF</i> 208	4.06	[124]
Rb ₂ CeF ₅	66.67	406.06	<i>oP</i> 32	4.35	[125]
RbCeF ₄	50.00	301.59	Pnma	5.04	[126]
CeF ₃	0.00	197.11	P $\bar{3}$ c1	6.16	[127]

4.4.2 Thermodynamic data for pure compounds

The Gibbs energy equation for the relevant compounds, presented in Eq. (4.1), comprises contributions from the enthalpy of formation, the absolute entropy at the reference temperature, and the heat capacity.

The Gibbs energy function of a pure compound is given by:

$$G(T) = \Delta_f H_m^\circ(298) - S_m^\circ(298)T + \int_{298}^T C_{p,m}(T)dT - T \int_{298}^T \frac{C_{p,m}(T)}{T} dT \quad (4.1)$$

where $\Delta_f H_m^\circ$ is the standard enthalpy of formation, S_m° is the standard absolute entropy, both evaluated at a reference temperature (298K) and $C_{p,m}$ is the isobaric molar heat capacity which is expressed as a polynomial as a function of temperature:

$$C_{p,m} = a + bT + cT^2 + dT^{-2} + eT^3 \quad (4.2)$$

where a, b, c and d are dimensionless constants and can be added if necessary.

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For the purpose of this work, pure components within this study, RbF, CeF₃ and PuF₃ were taken from Gurvich [68], and the Neumann Kopp rule was used to generate the C_p values of all intermediate compounds. $\Delta_f H_m^\circ$ and S_m° of intermediate compounds were optimised using CALPHAD method within the Factsage software and are given in **Table 4.3** with their thermodynamic properties.

Table 4. 3: Thermodynamic data of all pure components in this RbF-CeF₃ and RbF-PuF₃ study

Compound	T range (K)	$\Delta_f H_{298.15K}^\circ$ (J·mol ⁻¹)	$S_{298.15K}^\circ$ (J·K ⁻¹ ·mol ⁻¹)	$C_{p,m} = a + b \cdot T + c \cdot T^{-2} + d \cdot T^2$				Ref
				a	b	c	d	
RbF (s)	298.15 - 1000	-559700	77.70	42.34987	0.02600942	46610.33	7.981852E-9	Gurvich (1994) [68]
	1000 - 1220			221.1816091	-0.145753209	-46564553.48	3.95922E-5	
	1220 - 2000			71.0				
RbF (l)	298.15 - 580	-534789.47	100.83	42.34987	0.02600942	46610.33	7.981852E-9	Gurvich (1994) [68]
	580 - 948			43.0488533	0.017609851	2.08005E-8	1.25875E-5	
	948 - 3401			71.0				
CeF ₃ (s)	298.15 - 1710	-1688913	115.269	106.3991	-0.01977071	-885090.1	2.864938E-5	Gurvich (1994) [68]
	1710 - 2000			133.888				
CeF ₃ (l)	298.15 - 840	-1635787.64	144.379	106.3991	-0.01977071	-885090.1	2.864938E-5	Gurvich (1994) [68]
	840 - 950			4077.388916	-6.708013086	-416935089.9	0.003200064	
	950 - 2000			133.888				
PuF ₃ (s)	298.15 - 1700	-1552264.0	126.11	92.62	0.0288284	-747200	-1.85103E-6	Gurvich (1994) [68]
	1700 - 2000			146.44				
PuF ₃ (l)	298.15 - 770	-1514157.42	144.398	92.62	0.0288284	-747200	-1.85103E-6	Gurvich (1994) [68]
	770 - 950			2407.685645	-4.186583019	-209092191.7	0.002159831	
	950 - 2000			146.44				
Rb ₃ CeF ₈ (s)	298.15 - 1000	-3363426.961	413.369	233.44871	0.05825755	-745259.11	2.8673325556E-5	This work
	1000 - 1220			769.9439273	-0.457030337	-140578750.54	0.00014742598	
	1220 - 1710			319.3991	-0.01977071	-885090.1	2.864938E-5	
	1720 - 2000			346.888				
Rb ₂ CeF ₅ (s)	298.15 - 1000	-2873539.817	240.669	191.09884	0.03224813	-791869.44	2.8665343704E-5	This work
	1000 - 1220			548.7623182	-0.311277128	-94014197.06	0.00010783378	
	1220 - 1710			248.3991	-0.01977071	-885090.1	2.864938E-5	
	1720 - 2000			275.888				
RbCeF ₄ (s)	298.15 - 1000	-2296546.91	172.969	148.74897	0.00623871	-838479.77	2.8657361852E-5	This work
	1000 - 1220			327.5807091	-0.165523919	-47449643.58	6.824158E-5	
	1220 - 1710			177.3991	-0.01977071	-885090.1	2.864938E-5	
	1720 - 2000			204.888				
RbCe ₂ CeF ₇ (s1)	298.15 - 1000	-4011466.171	273.238	255.14807	-0.013532	-1723569.87	5.7306741852E-5	This work

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	1000 – 1220			433.9798091	-0.185294629	-48334733.68	9.689096E-5	
	1220 – 1710			283.7982	-0.03954142	-1770180.2	5.729876E-5	
	1720 – 2000			338.776				
RbCe ₂ CeF ₇ (s2)	298.15 – 1000	-4000734.671	283.238	255.14807	-0.013532	-1723569.87	5.7306741852E-5	This work
	1000 – 1220			433.9798091	-0.185294629	-48334733.68	9.689096E-5	
	1220 – 1710			283.7982	-0.03954142	-1770180.2	5.729876E-5	
	1720 – 2000			338.776				
Rb ₃ PuF ₆ (s)	298.15 – 1000	-3239441.738	419.21	219.66961	0.10685666	-607369.01	-1.827084444E-6	This work
	1000 – 1220			756.1648273	-0.408431227	-140440860.44	0.00011692557	
	1220 – 1700			305.62	0.0288284	-747200	-1.85103E-6	
	1720 – 2000			359.44				
Rb ₂ PuF ₅ (s)	298.15 – 1000	-2736382.546	261.51	177.31974	0.08084724	-653979.34	-1.835066296E-6	This work
	1000 – 1220			534.9832182	-0.262678018	-93876306.96	7.733337E-5	
	1220 – 1700			234.62	0.0288284	-747200	-1.85103E-6	
	1720 – 2000			288.44				
RbPuF ₄ (s)	298.15 – 1000	-2180688.646	168.81	134.96987	0.05483782	-700589.67	-1.843048148E-6	This work
	1000 – 1220			313.8016091	-0.116924809	-47311753.48	3.774117E-5	
	1220 – 1700			163.62	0.0288284	-747200	-1.85103E-6	
	1720 – 2000			217.44				
RbPu ₂ F ₇ (s1)	298.15 – 1000	-3745396.545	294.92	227.58987	0.08366622	-1447789.67	-3.694078148E-6	This work
	1000 – 1220			406.4216091	-0.088096409	-48058953.48	3.589014E-5	
	1220 – 1700			256.24	0.0576568	-1494400	-3.70206E-6	
	1720 – 2000			363.88				
RbPu ₂ F ₇ (s2)	298.15 – 1000			227.58987	0.08366622	-1447789.67	-3.694078148E-6	This work
	1000 – 1220			406.4216091	-0.088096409	-48058953.48	3.589014E-5	
	1220 – 1700			256.24	0.0576568	-1494400	-3.70206E-6	
	1720 – 2000			363.88				

4.5 Thermodynamic modelling of the liquid solution

4.5.1 Thermodynamics of Molten Salt Solutions

Computational modelling is essential for evaluating chemical equilibria, reaction kinetics, transport properties, and thermochemical behaviour in complex multicomponent, multiphase systems. This complexity is further compounded by compositional changes over time, as will occur in a Molten Salt Fast Reactor (MSFR), where fissile ions within the bulk fuel salt undergo fission, producing a range of new fission product isotopes. Accurate experimental data are required to

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define the parameters used in such models; however, these data are often unavailable or experimentally challenging to obtain. Consequently, to enable reliable predictions in complex systems, it is necessary to first develop robust thermodynamic descriptions of simpler systems—for example, those present at Beginning of Life (BOL) conditions.

The computational framework is based on Gibbs free energy minimisation, which can be implemented using modern software tools such as FactSage. For multicomponent systems, thermodynamic modelling draws upon data from pure end-member components, available experimental measurements, and optimised interaction parameters. To compute phase equilibria and possible chemical reaction pathways involving molten salt solutions, the thermodynamic properties of solution phases must be defined as functions of composition, temperature, and pressure. Accordingly, a range of thermodynamic models have been developed to describe organic and inorganic systems across solid, liquid, and gaseous phases. While gas phases are typically fully miscible, solid and liquid phases often exhibit phase separation (i.e. immiscibility). Although non-ideal gas behaviour can be addressed through various modelling approaches, gas-phase effects are not considered in the present work due to the high-temperature (>400 °C), ambient-pressure conditions characteristic of MSFR operation. These effects, however, should be investigated and incorporated in future studies, should the molten salt system under consideration demonstrate promising characteristics for MSFR fuel and design applications. In general, for all solution phases, the Gibbs free energy, G , is expressed by the following equation:

$$G = G^{\circ} + \Delta G_{mix}^{ideal} + \Delta G_{mix}^{excess} \quad (4.3)$$

where G° is the standard Gibbs energy of the pure components within the solution phase of interest, ΔG_{mix}^{ideal} is the ideal Gibbs energy of mixing and ΔG_{mix}^{excess} is the excess Gibbs energy of mixing that introduces the non-ideal contributions into the MS solution.

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Gibbs energy minimisations are performed computationally for complex systems and can determine true chemical equilibrium once the data from all phases are input into the model. The Gibbs energy is hence described as:

$$G = \sum_i n_i \bar{G}_i \quad (4.4)$$

where n_i is the number of moles of component i , and $\bar{G}_i$ is the calculated or known chemical potential of component i , for a given set of fixed constraints, such as P , T and overall composition. In the following section, the framework of the most relevant thermodynamic model used to best describe molten salt solutions that exhibit Short-Range-Ordering (SRO) is further explained. The C_p can be derived mathematically by a second order partial derivative of the Gibbs energy and further validated by experimental measurement.

4.5.2 Thermodynamic model details

The modified quasi-chemical model quadruplet approximation (MQMQA), proposed by [60] was used to model the excess Gibbs energy of the liquid phase. The quadruplet model consists of two sub-lattices, one consisting of cations A and B (representing M³⁺ and Rb⁺) and anion F⁻ (in this work only fluoride anion is present). The quadruplet is the fundamental unit in this model. In previous models, i.e. QCM pair approximation, the first-nearest neighbours (FNN) interactions rather than the second-nearest neighbours (SNN) were modelled to be the dominant influence on the excess terms, shown in **Fig. 4.1**. The quadruplet approximation is updated and treats FNN and SNN interactions simultaneously for determining optimised excess parameters of the liquid solution.

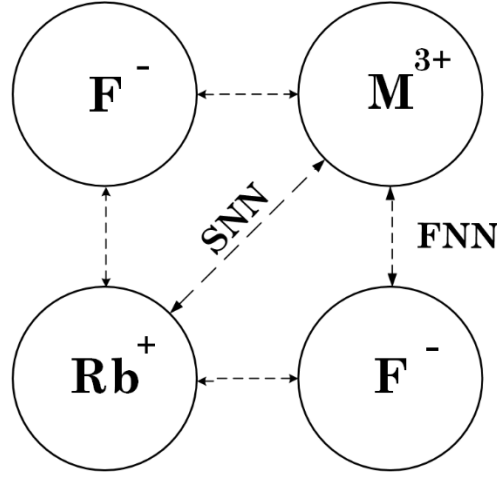
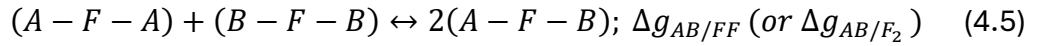
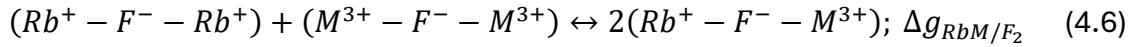


Fig. 4. 1: Schematic of one quadruplet model illustrating first-nearest neighbour (FNN) and the second-nearest neighbour (SNN) with two cations (Rb^+) and (M^{3+} , where $M = Ce, Pu$) and two anions both (F^-) in this case.

The transfer reaction between FNN and SNN pairs are expressed as:



or



$\Delta g_{RbM/F_2}$ is an empirical parameter and may be composition dependant, if $\Delta g_{RbM/F_2} = 0$ then random mixing occurs, if $\Delta g_{RbM/F_2} < 0$, then Equation 8 is displaced to the right with ($Rb^+ - F^- - M^{3+}$) pairs becoming predominant.

The Gibbs energy change $\Delta g_{AB/F_2}$ associated with the SNN-FNN reaction is given by:

$$\Delta g_{RbM/F_2} = \Delta g_{RbM/F_2}^0 + \sum_{i \geq 1} g_{RbM/F_2}^{i0} x_{RbM/F_2}^i + \sum_{j \geq 1} g_{RbM/F_2}^{j0} x_{RbM/F_2}^j \quad (4.7)$$

Where $\Delta g_{RbM/F_2}^0$, g_{RbM/F_2}^{i0} and g_{RbM/F_2}^{j0} are composition independent coefficients that may vary with temperature. Note that the terms with subscript RbM/F_2 and MRb/F_2 represent the same pairs and can be used interchangeably. x_{RbM/F_2}^{ij} is composition dependant function, defined as the fraction to cation-cation pair mole fractions X_{RbRb/F_2} , X_{RbM/F_2} and X_{MM/F_2} :

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$$X_{RbM/F_2}^{Rb} = \frac{X_{RbRb/F_2}}{X_{RbRb/F_2} + X_{RbM/F_2} + X_{MM/F_2}} \quad (4.8)$$

As the composition of RbF-MF₃ binary systems changes, the quadruplet approximation model must maintain other parameters to satisfy the conservation of charge whilst simultaneously considering how the FNN and SNN coordination number varies. By assuming the cation SNN coordination number and the charges of cation/anion remains constant, the anion SNN coordination numbers are fixed in the quadruplet by:

$$\frac{q_{Rb}}{Z_{RbM/F_2}^{Rb}} + \frac{q_M}{Z_{RbM/F_2}^M} = \frac{q_F}{Z_{RbM/F_2}^F} + \frac{q_F}{Z_{RbM/F_2}^F} \quad (4.9)$$

Where q_i are the charges of anions and cations, and Z_{RbM/F_2}^i are the SNN coordination number of the respective ion in each quadruplet. For each both end members, the quadruplet formations include (M³⁺-F⁻-M³⁺), (Rb⁺-F⁻-Rb⁺), (Rb⁺-F⁻-M³⁺) SNNs. Their excess Gibbs energy expressions are expressed as $\Delta g_{RbRb/F_2}$, $\Delta g_{RbM/F_2}$ and $\Delta g_{MM/F_2}$.

The current work introduces M_{vi}^{3+} (with coordination number in indices) into the pure liquid MF₃ as the same complex and surrogate complexes were identified in Raman spectroscopy studies with MF₃ and AF mixtures (A = Li, Na, K; M = Ce, Pu). This permits one composition of second nearest neighbour-short range ordering (SNN-SRO). There was no evidence for formation of M_{iv}^{3+} four-coordinated M³⁺ within melts, but there was for the six-coordinated complex, corresponding to the [MF₆]³⁻ “complex-anion”.

Following this methodology, the following complexes and [MCl₆]³⁻ have SRO at compositions $X(MF_3)$ at 0.25. The results show that this model can satisfactorily reproduces all experimental phase diagram data and predicted enthalpy of mixing.

As this model incorporates Ce and Pu cations in each system, pure CeF₃ and PuF₃ liquid becomes a mixture of M_{vi}^{3+} cation species and respectively F⁻ anions. From the Raman spectroscopy data produced by [114] in MF₃, M_{vi}^{3+} is the dominant species. Although only a single six-coordinated complex species was modelled in the present melt, the methodology was intentionally developed to remain

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consistent with previous work, thereby ensuring compatibility with future modelling efforts involving higher-order systems in which the six-coordinated complex is also expected to persist.

The resulting molten salt binary system has the Gibbs free energy calculation by the Factsage software by summing the Gibbs free energies of the various quadruplets along with the energy contributed by the configurational entropy resulting from the distribution of the quadruplets on the lattice sites as expressed below:

$$G = \sum_{i=M_{vi}} \sum_{j=Rb} \sum_{k=F} n_{ij/kk} g_{ij/k}^0 - T\Delta S^{config} \quad (4.10)$$

Where $n_{ij/kk}$ is the number of moles of the ij/kk quadruplet, $g_{ij/k}^0$ is the molar Gibbs free energy of the ij/k quadruplet, and ΔS^{config} is the configurational entropy of mixing. A definitive mathematical description of the entropy term is not presently established; however, an appropriate expression was proposed by Pelton *et al* (2000). The approximation was later improved by [28] to treat FNN and SNN SRO. $n_{ij/kk}$ is the number of moles of quadruplets, which requires a minimisation of the Gibbs free energy of the molten salt binary solution at a known temperature, pressure and composition – this embodies the equilibrium configuration of both the FNN and SNN. Although the SNN numbers are not used to physically characterise the complexes within the salt solution, they are model parameters allowing them to define the composition of which maximum SRO occurs. This is constrained by charge neutrality, by Equation 4.9 and following Z numbers used in this model in **Table 4.4**.

Table 4. 4: SNN “coordination numbers” for quadruplets ABXX (with X = F) used in the MQMQA for the liquid to model SRO at compositions X(MF₄) at 0.25 for [MF₆]³⁻.

A	B	Y	$Z_{AB/YY}^A$	$Z_{AB/YY}^B$	$Z_{AB/YY}^Y$	$Z_{AB/YY}^Y$
Rb	Ce _{vi}	F	2.4	7.2	2.4	2.4
Rb	Pu _{vi}	F	2.4	7.2	2.4	2.4

The modified solution model builds on the composition dependent Gibbs energy exchange Eq. 10 as there are two cations in the molten solution; Rb⁺ and M³⁺, there

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are the proposed two; Rb⁺, and M_{vi}^{3+} . Mole fraction pairs given in Eq. 8 by mole fraction pairs, are now used by composition variable $\chi_{AB/YY}$ or χ_{AB/Y_2} , accordingly proposed as the following:

$$\chi_{RbM_{vi}/F_2} = X_{Rb_2/F_2} \quad (4.11)$$

$$\chi_{M_{vi}Rb/F_2} = X_{(M_{vi})_2/F_2} \quad (4.12)$$

As Equation 10 represents the total Gibbs free energy on the overall system as a given composition and temperature, the expression for the configurational entropy of mixing (ΔS^{conf}) necessitates FNN pair fractions to mitigate convergence between quadruplets and other sets of quadruplets. The parameter ζ is introduced which is defined as the number of quadruplets emanating from a FNN pair, in this case, a Rb⁺-F⁻ or M³⁺-F⁻ pair. In other molten salt models using the improved MQMQA, authors have varied ζ , normally to account for the reciprocal systems containing significant differences of anionic radii, such as F⁻ and CO₃²⁻. In this work, ζ has been kept equal to 2.4, as proposed by Chartrand et al. (2011) [55] for Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺//F⁻, Cl⁻ reciprocal system.

Lastly, the $\Delta g_{RbM/F_2}$ of all the quadruplets were manually optimised without the use of Optisage software to fit the previous and new experimental phase diagram data explored in this work – alongside the anticipated enthalpy of mixing. The coefficients are usually expressed as A + BT, where A and B are optimised individually to achieve the possible fit to the data. In this work, as the RbF-MF₃ binary system is more complex, exhibiting two different eutectics, rather than a simple singular eutectic found in the NaF-RbF system, more coefficients were introduced, A - typically being the constant enthalpic term, and the latter terms being entropic that vary with temperature, such as:

$$\Delta g_{RbM/F_2} = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E \cdot T^3 \quad (4.13)$$

In this work, to preserve the overall fit of the enthalpy mixing terms and reproduce the general minimum at $X(MF_3) = 0.4$, the entropic contributions were iteratively refined to optimise the fitting of the liquidus curves in the phase diagram.

4.5.3 Empirical method for enthalpy of mixing

Thermochemical data are equally essential as phase equilibrium data for the accurate optimization of thermodynamic parameters in solution phases. However, no experimental measurements of the mixing enthalpy have been reported for the AlkF-MF₃ (Alk = Li, Na, K, Rb, Cs, M = Ce, Pu) binary melts. Consequently, an empirical estimation method was employed in this study similar to Schorne-Pinto et al. (2022) [58] but for the fluoride systems. This method explicitly examines the intrinsic correlation between the experimental and calculated mixing enthalpy available in the literature of binary molten salt systems and their respective ionic parameters, typically expressed as a function of ionic radii or related metrics as explored by Davis et al. [128]. As demonstrated in previous studies in the summary made by Li et al. (2017) [129], the mixing enthalpies of AlkF-LnF₃ (Ln = La, Nd, Gd, Y, Yb, Al) binary systems can similarly be predicted using the following equation:

$$\delta_{12} = \frac{[r_A^+ + r_F^-] - [r_M^{3+} + r_F^-]}{[r_A^+ + r_F^-] \cdot [r_M^{3+} + r_F^-]} \quad (14)$$

Where r_A^+ is the ionic radius of the alkali cation in the systems, r_M^{3+} is the ionic radii of the trivalent metal cation and r_F^- is the ionic radii of fluorine in each binary system. An assessment of existing ΔH^M datasets as a function of ionic size parameter, δ_{12} (highlighted in **Fig. 4.2-6**) confirmed the presence of a comparable trend. One trend common to all assessed mixtures, including AF-LnF₃, where A = Li, Na, K, Rb, Cs binary systems, that with heavier Alk cation for common anion systems, i.e. Li > Na > K > Rb > Cs, ΔH^M becomes more negative. Another trend to AX -MX₃ binary mixtures, is that the minimum ΔH^M lies in the X(MF₃) = 0.4 mole fraction region, indicative of stronger SRO in the alkali metal halide-rich composition.

The literature data is presented in **Figs. 4.2-4** and demonstrate how the final linear prediction method was used to calculated values for the RbF-CeF₃ and RbF-PuF₃ system.

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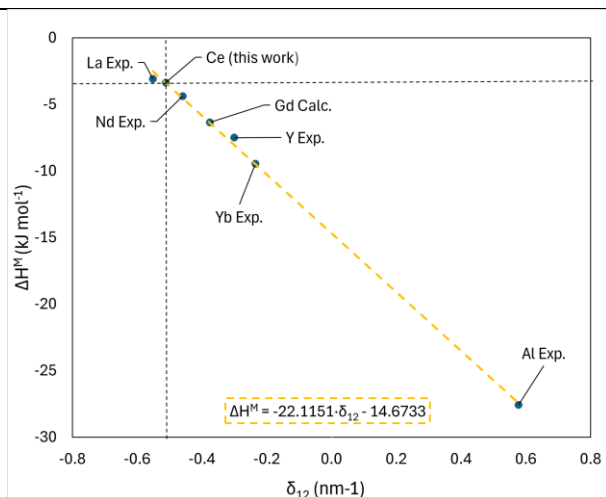


Fig. 4. 2: ΔH^M experimental and calculated values for LiF-LnF₃ mixtures available in the literature as function of δ_{12} ionic size parameter.

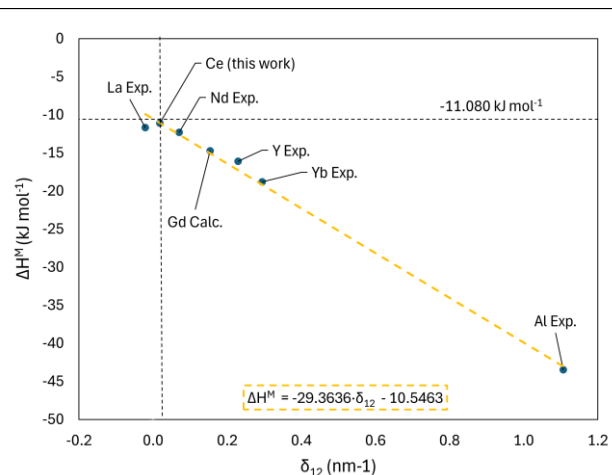


Fig. 4. 3: ΔH^M experimental and calculated values for NaF-LnF₃ mixtures available in the literature as function of δ_{12} ionic size parameter.

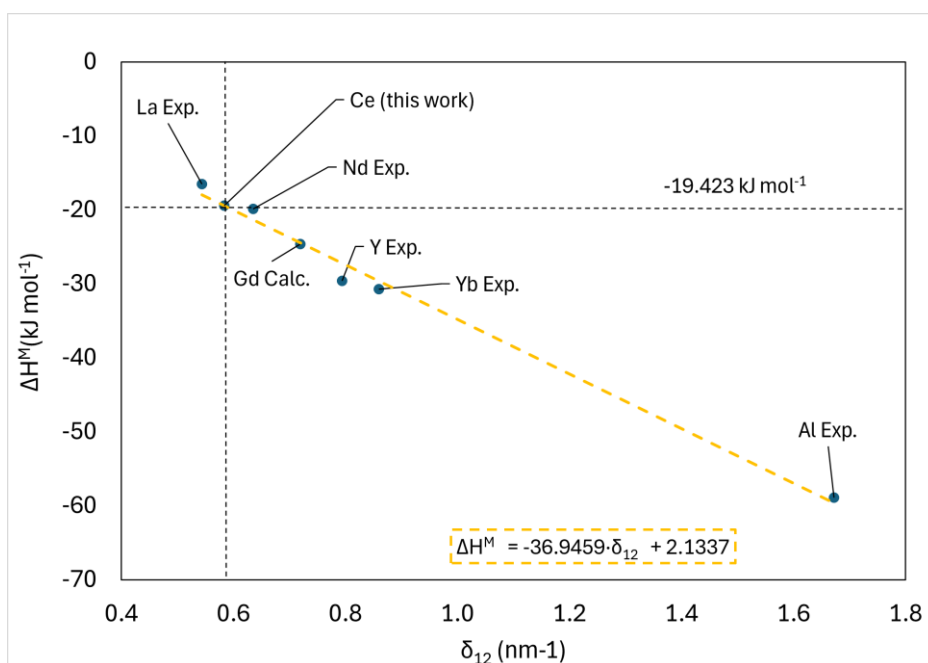


Fig. 4. 4: ΔH^M experimental and calculated values for KF-LnF₃ mixtures available in the literature.

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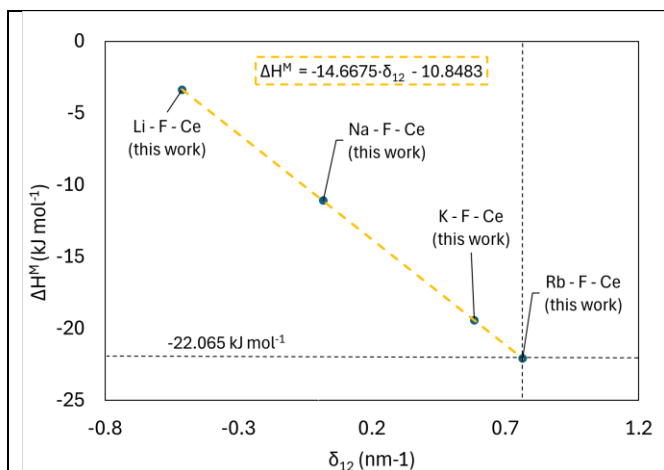


Fig. 4. 5: ΔH^M calculated values for RbF-CeF₃ in this work as function of δ_{12} ionic size parameter.

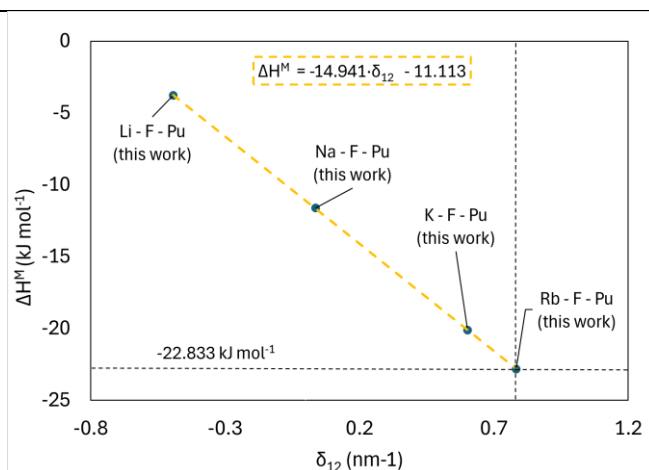


Fig. 4. 6: ΔH^M calculated values for RbF-PuF₃ mixtures in this work as function of δ_{12} ionic size parameter.

4.6 Experimental

4.6.1 TGA & DSC Instrumentation and methodology

The TGA-DSC unit used for the experiments is a NETZSCH STA 449 F3 Jupiter. This instrument allows simultaneous Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements. Measurements are carried out, with production of a DSC curve, and data are treated using Netzsch software Proteus®, see Netzsch (2008) [67].

The TGA-DSC measurements are based on the record of temperature and time during heating or cooling and the difference between a reference and the measured sample both in crucibles. The sample carrier of the unit can host two crucibles. The furnace which surrounds the crucibles can *slide* up to insert or remove the crucibles when needed. When the furnace is fully closed, the experiment can be run, and during the experiment, heat is generated inside the cell. A protective inert gas (Ar) is flown (200 ml min⁻¹) inside the cell during all the operations.

An established methodology is employed in order to obtain consistent and accurate results. Calibrations are done according to the crucible type used, the temperature domain and sensitivity. KNO₃, KClO₄, CsCl, BaCO₃ and Ag were used for the ΔH calibrations, as these do not react or alloy with nickel crucible unlike more

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traditional DSC calibrations standards such as gold and zinc can do with Ni-201 and SUS316L.

Prior to calibration, a blank run with an empty crucible was performed to establish the baseline. With frequent TGA/DSC use, baseline drift was observed; however, the high sensitivity of the custom crucibles employed in this study enabled clear and easily interpretable thermal peaks. The cycles are programmed with different temperature ramps and cooling cycles to show if super-cooling effects were significant or phase change temperatures were heating-rate dependant.

Calibration curve used for DSC fluoride experiments, utilising Netzsch calibration software are reported in **Fig. 4.7 and 4.8**. **Table 4.5** provides the calculated temperature corrections reported by Netzsch for the 5 suggested standards.

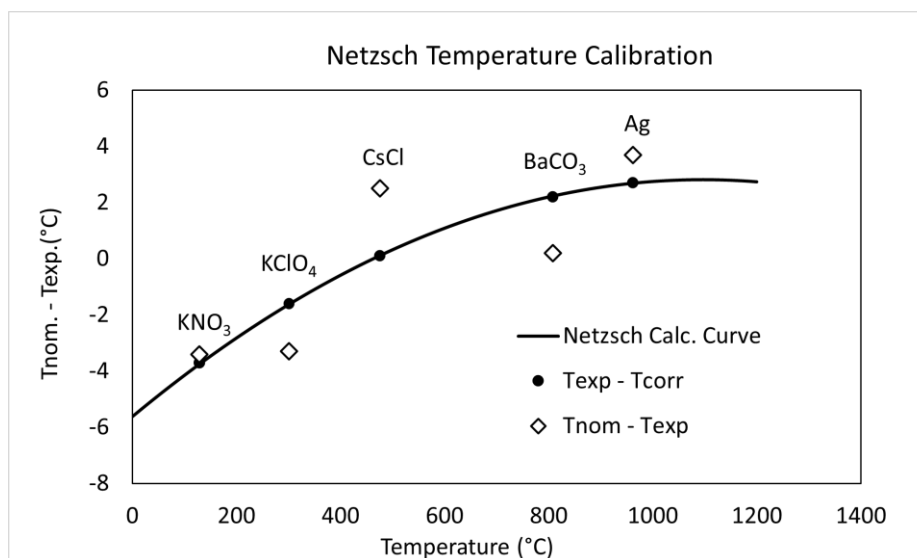


Fig. 4. 7: Calibration curves used for DSC fluoride experiments Temperature calibration, correction Curve (°C) = $10^{-3} \cdot b_0 + 10^{-5} \cdot b_1 \cdot T_{exp.} + 10^{-8} \cdot b_2 \cdot T_{exp.}^2$,
 $b_0 = -5620.2$, $b_1 = 1538.6$, $b_2 = -701.8$

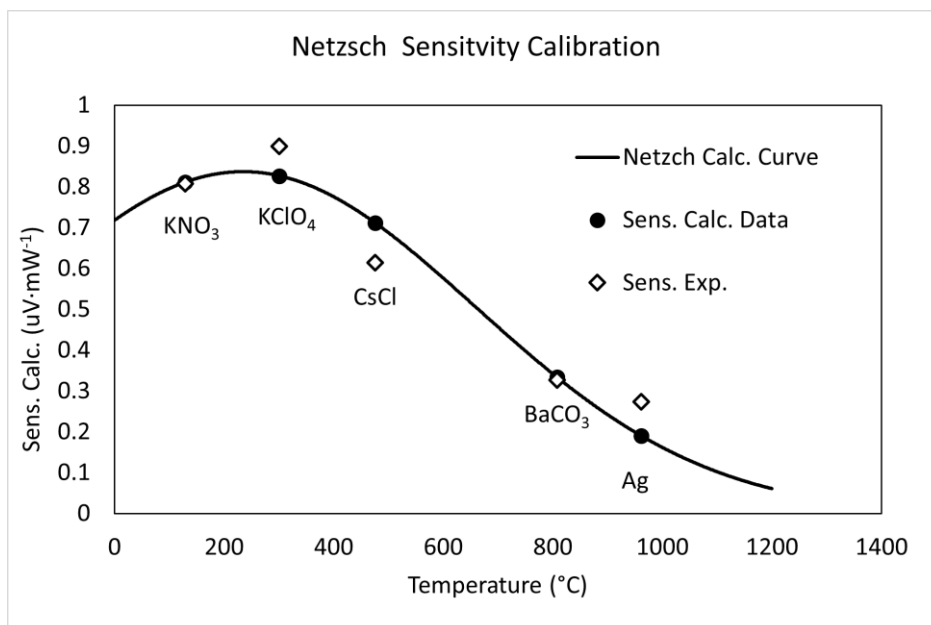


Fig. 4. 8: Sensitivity calibration, data from Netzsch Calibration Software, Sensitivity Curve ($\text{uV} \cdot \text{mW}^{-1}$) = $(P_2 + P_3 + P_4 \cdot z^2 + P_5 \cdot z^3) \cdot \exp(-z^2)$, with $z = (T - P_0)/P_1$, $P_0 = 300.79999$, $P_1 = 605.82794$ and $P_2 = 0.82741$, $P_3 = -0.18496$, $P_4 = 0.00000$, $P_5 = 0.0000$, from Netzsch database.

From the manual, the curve is acceptable if the fitted curve goes through all points on the graph and the T_{nom} (Nominative Temperature or temperature from the literature) and $T_{\text{corr.}}$ (Corrected temperature, from the calibration curve) are within 1-3°C of each other, see **Table 4.5**.

Table 4. 5: Netzsch calculated temperature corrections for DSC temperature calibration.

Standard	$T_{\text{nom.}}$ (°C)	$T_{\text{exp.}}$ (°C)	$T_{\text{corr.}}$ (°C)
KNO ₃	128.7	132.1	128.4
KClO ₄	300.8	304.1	302.5
CsCl	476.0	473.5	473.6
BaCO ₃	808.0	807.8	810.0
Ag	961.8	958.1	960.8

After these preliminary tests, a crucible (**Fig. 4.9**) loaded with sample can be placed on the sample carrier in the furnace, the gas turned on, and the cycles run. Four heating cycles are ran, 10 °C min⁻¹, 10 °C min⁻¹, 8 °C min⁻¹, 5 °C min⁻¹ (first heating cycle is disregarded to ensure full melting and subsequent mixing) and three cooling cycles, 10 °C min⁻¹, 8 °C min⁻¹ and 5 °C min⁻¹. During the cycle and until the machine

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comes back to room temperature, the furnace is locked to protect the operator – the hermetic seal of the crucible also provides protection to the internal components of the furnace from fluoride salt vapour. At the end of the measurement, two curves are obtained from the TGA and the DSC. TGA measurement is a type of measurement that is based on differences in weight during temperature heating and cooling cycles by Byrn *et al.* (2017) [130]. The machine has an internal balance which records mass during cycles (if the crucible was open or mechanically failed, mass loss occurred). For the DSC, the quantity measured is the difference in heat flow released or absorbed between the reference empty crucible and the crucible filled with sample. When a chemical reaction or a phase transition takes place in the sample for example, heat is released (exothermic) or absorbed (endothermic), which results in a massive difference between the reference crucible and the sample, materialised by a peak on the DSC curve.

The precision of the TGA thermometer is ± 0.001 °C as per Charsley *et al.* (2019) [131], so the main error due to the TGA unit is in the calibration process, which is done manually, and involve the record of the standard transition and extrapolation of T_{tr} .

4.6.2 Crucible choice & design

The selection of an appropriate crucible is one of the most critical factors in ensuring reliable TGA-DSC measurements. An ideal crucible must exhibit high thermal conductivity and chemical inertness with both the sample and the DSC sensor assembly. As no commercially available crucibles exist for the specific measurement of molten salts, previous efforts made by Beneš *et al.* (2010) [63] and Piro *et al.* (2021) [132] explored and designed their own crucibles. In this work, custom crucibles were fabricated specifically for molten fluoride salt analysis, tailored to the dimensional constraints of the TGA-DSC apparatus, while prioritising a minimal mass design. They featured a flat base to ensure optimal thermal contact

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with the DSC holder and were suitable for operation across the required temperature range (0–1000 °C).

DSC sensitivity is directly influenced by the enthalpy difference and is optimised when the thermal response is not dominated by the crucible's thermal inertia. Enhanced sensitivity is achieved when the crucible mass is kept small relative to the sample mass, thereby minimising heat capacity effects. High thermal conductivity of the crucible material also plays a key role. In this study, the total crucible mass was 330 mg, significantly lower than typical commercial crucibles, which range from 1 to 10 g and are generally unsuitable for high-temperature fluoride salt analysis. Other research institutions have also resorted to designing custom crucibles for molten salt studies; however, these efforts often involved trade-offs in other performance parameters to remain within system design constraints.



Fig. 4. 9: Sealed custom-made crucibles developed at Lancaster University NETZSCH STA 449 F3 Jupiter crucible holder with protective alumina disks post-run



Fig. 4. 10: Crucible post-experiment (81.2 mol% RbF- 18.8 Mol% CeF₃) sanded open and inspected for corrosion.

The newly developed crucible design was employed in these experiments, enabling the use of small salt quantities (>20 mg) due to its compact internal volume (21.5 mm³), while significantly enhancing the sensitivity of TGA-DSC measurements. This crucible was specifically engineered at Lancaster University for use with actinide and lanthanide. The design was tailored to address the specific requirements of fluoride and chloride salts, particularly with respect to sealing integrity, thermal conductivity, chemical compatibility, corrosion resistance, and high-temperature performance.

Given that fluoride salts are hygroscopic, air-sensitive, and potentially toxic to both users and the environment, it is essential to maintain them in sealed environments to prevent contamination by atmospheric oxygen or water vapour. Effective sealing is therefore critical, not only to protect the sample from environmental exposure but also to prevent compositional shifts due to volatilisation and mass loss during heating.

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Moreover, since the primary investigations on fluoride salts involve their melting behaviour and high-temperature phase properties, the crucible must perform reliably up to at least 1000 °C. Ni-201 was selected as the crucible material for its high-temperature and corrosion resistance, while SUS316L stainless steel was used for the lid. Using matching alloys for both crucible and lid components led to galling during sealing and leakage at elevated temperatures due to volatilisation.

4.6.3 Reagent preparation & handling

The reagents used are:

Cerium trifluoride (CeF₃) anhydrous powder from Alfa Aesar (as supplied, 10 g batch, purity 99.9%)

Rubidium fluoride (RbF) powder from Alfa Aesar (as supplied, 2 g batch, purity 99.975%).

For TGA-DSC calibration the standards reagents used are given in Table 4 prior DSC fluoride experiments.

Table 4. 6: TGA-DSC standards reagents nominative properties as given in Netzsch (2008) [67].

Calibrant	Temperature (°C)	Enthalpy (kJ mol ⁻¹)	Purity (%)
KNO ₃	128.7	5.0551	99.99
KClO ₄	300.8	14.533	99.9999
CsCl	476.0	2.896	99.99
BaCO ₃	808.0	18.727	99.997
Ag	961.0	11.296	99.99

They were systematically used to calibrate the temperature using transient phase changes. The Netsch software uses polynomial-exponential equations to fit the data to highly accurate measurements between calibrant temperatures and extrapolates outside calibrant temperature, which provides less accurate data. In addition, the enthalpy of phase transition was standardised. Calibrations for T and for ΔH are subsequently performed and consequently calibrations for C_p 's are inferred. Precision issues are treated in the discussion Section.

Purification of hygroscopic salts like RbF is mandatory. Because of their strong interaction, water as well as oxygen need to be removed from the fluoride salts. All

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experiment needs to be carried out in H₂O-free/O₂-free atmosphere. In addition, the fluorides salts should be anhydrous.

A standard vacuum oven was found insufficient for salt dehydration, as it lacked the ability to isolate the sample post-drying, resulting in air exposure upon opening. To overcome this, a Schlenk flask connected to a Schlenk line was employed, enabling airtight transfer of the dried salt to the glovebox. Once maximum vacuum is reached in a static system, liberated water vapour may remain in the headspace above the sample and risk reabsorption upon re-pressurisation. This risk is mitigated in the Schlenk line setup by rapid purging the flask with dry argon, which continuously flushes water vapour away as pressure is restored. This purge–vacuum cycle was repeated over 72 hours to ensure sufficient dehydration. Heating was provided by a temperature-controlled sand bath set to 250 °C.

The use of a Schlenk flask and line enables isolation of the contents at the valve following the 72-hour cyclic drying process, since the operation is carried out in a fume hood, external to the glovebox. Once drying is complete and the flask is isolated, it can be transferred to the glovebox, ensuring that the salt will never have contact with air, thus achieving no risk of moisture reabsorption.

All crucibles and lids were cleaned by immersion in a 1:1 ethanol–acetone solution and treated in an ultrasonic bath for 60 minutes at room temperature. After discarding the solution, they were rinsed with distilled water and subsequently placed in 100% anhydrous methanol for a second 60-minute ultrasonic treatment. Finally, once the bulk methanol was discarded, and crucibles and lids were dried in a 60°C oven for 4 hours to ensure complete removal of residual methanol.

The glovebox maintains a continuous circulation of argon under slight positive pressure to preserve inert conditions. However, with argon circulators turned off, even small pressure fluctuations affect balance stability, particularly for mass measurements under ~20 mg. Therefore, for improved accuracy and reproducibility, all weighing was performed outside the glovebox. Pure salts were added to the crucible using an anti-static spatula. The crucible and contents were

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then placed in a sealed glass vial, removed from the glovebox, and weighed incrementally until the desired composition was reached.

Once the desired molar ratio was obtained, the crucible was sealed using a hand-operated hydraulic press to fit the tapered lid, forming a hermetic seal. The sealed crucible was then transferred directly to the NETZSCH STA 449 F3 Jupiter furnace, eliminating risk of moisture reabsorption from air exposure. This weighing protocol avoids the electrostatic interference and pressure instability commonly encountered in dry gloveboxes, thereby enhancing measurement reliability.

Prior to initiating the heating and cooling cycles in the furnace, the unit was purged for approximately 30 minutes to remove residual H₂O/O₂ to reduce oxidation of the outer crucible walls which ensured structural integrity. Small 10 mg alumina disks were placed between the platinum/rhodium DSC holder and the underside of the Ni-201 crucible to prevent any metal – metal interaction and ensure adequate heat flow. All calibrations carried out prior as discussed in Section 5.1 also incorporated the alumina disks to ensure repeatability. NETZSCH STA 449 F3 Jupiter was calibrated to ensure accurate temperature readings, and any deviations were promptly addressed. After the experiment, the crucible is allowed to cool under the furnace circulation before being removed from the furnace for analysis.

4.7 Results & Discussion

4.7.1 Phase Equilibria measurements of the RbF-CeF₃ system

The DSC curves recorded so far allow accurate measurements of the phase change. The DSC data present consistent values from heating with different heating rates and slight variance from cooling with different cooling rates due to supercooling phenomena. A phase transition, which can be melting, solidification, change in isomorphic state and chemical decomposition in the investigated temperature domain is characterised by transition temperature. The heating cycle data were used for phase equilibria points in this study, as it was noted the

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interpolated phase transition temperatures were not heating rate dependant and produce highly consistent results, highlighted in **Fig. 4.11**.

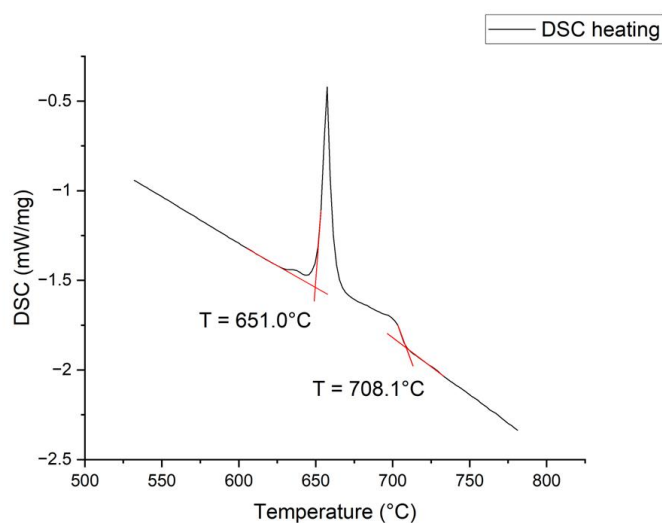


Fig. 4. 11: Raw DSC data RbF-CeF₃ (87.7 mol% – 12.3 mol%), heating rate as 5°C min⁻¹.

The invariant transformation points observed for the system RbF-CeF₃ system are compared with those gained in the estimation study of Fedorov (1999) [119] in **Table 4.7**. These points concern the RbF rich side of the phase diagram. Data are comparable within the error of 10°C on the transition temperature and 0.01 on the molar fraction.

Table 4. 7: Invariant points of the calculated RbF-CeF₃ system in this study.

Reaction in RbF-CeF ₃ system	Calculated and experimental invariant points		References
	T (°C)	X(CeF ₃)	
Liquid → RbF + Rb ₃ CeF ₆	625	0.14	Fedorov (1999) [119]
	651	0.14	This work
Liquid → Rb ₃ CeF ₆	758	0.25	Fedorov (1999) [119]
	755	0.25	This work
Rb ₃ CeF ₆ → RbF + Rb ₂ CeF ₅	475	0.25	Fedorov (1999) [119]
	461	0.25	This work
Liquid → Rb ₃ CeF ₆ + RbCeF ₄	690	0.33	Fedorov (1999) [119]

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	675	0.33	This work
$\text{Rb}_3\text{CeF}_6 + \text{RbCeF}_4 \rightarrow 2\text{Rb}_2\text{CeF}_5$	626	0.33	Fedorov (1999) [119]
	548	0.33	This work
$\text{Liquid}' + \text{CeF}_3 \rightarrow \text{Liquid}' + \text{RbCe}_2\text{F}_7 (\beta)$	938	0.50	Fedorov (1999) [119]
	870	0.50	This work
$\text{Liquid}' + \text{RbCe}_2\text{F}_7 (\beta) \rightarrow \text{Liquid}' + \text{RbCe}_2\text{F}_7 (\alpha)$	866	0.50	Fedorov (1999) [119]
	800	0.50	This work

Table 4. 8: Invariant points of the calculated RbF-PuF₃ system in this study.

Reaction in RbF-PuF ₃ system	Calculated invariant points		References
	T (°C)	X(PuF ₃)	
$\text{Liquid} \rightarrow \text{RbF} + \text{Rb}_3\text{PuF}_6$	642	0.16	This work
$\text{Liquid} \rightarrow \text{Rb}_3\text{PuF}_6$	768	0.25	This work
$\text{Rb}_3\text{PuF}_6 \rightarrow \text{RbF} + \text{Rb}_2\text{PuF}_5$	435	0.25	This work
$\text{Liquid} \rightarrow \text{Rb}_3\text{PuF}_6 + \text{RbPuF}_4$	671	0.33	This work
$\text{Rb}_3\text{PuF}_6 + \text{RbPuF}_4 \rightarrow 2\text{Rb}_2\text{PuF}_5$	537	0.33	This work
$\text{Liquid}' + \text{PuF}_3 \rightarrow \text{Liquid}' + \text{RbPu}_2\text{F}_7 (\beta)$	720	0.50	This work
$\text{Liquid}' + \text{RbPu}_2\text{F}_7 (\beta) \rightarrow \text{Liquid}' + \text{RbPu}_2\text{F}_7 (\alpha)$	830	0.50	This work

4.7.2 Calculated phase diagram of the RbF-CeF₃ and RbF-PuF₃ systems

Data extracted from the DSC curves were used to construct an approximate RbF-CeF₃ phase diagram based on the available experimental results (**Fig. 4.12**). These data, particularly within the composition range of 0-30 mol% CeF₃, were straightforward to interpret and were subsequently used to support the

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construction of the corresponding RbF-PuF₃ phase diagram. It should be noted that data beyond 35 mol% CeF₃ may be unreliable, as complete melting of the binary mixture might not have been achieved due to the high liquidus temperature on the CeF₃-rich side and the operational temperature limits of both the TGA/DSC instrument and the crucible. Two eutectic points were identified experimentally. The compound Rb₃CeF₆, which exhibits congruent melting and has already been reported by Fedorov (1999) [119], is located at 25.0 mol% CeF₃ with a liquidus maximum of 756 °C. A second eutectic occurs at 33.8 mol% CeF₃ and 690 °C.

Beyond this region, experimental data are sparse, allowing only partial or approximate definition of the remaining phase equilibria. However, within the context of molten salt reactor (MSR) applications, such CeF₃-rich compositions would be of limited interest due to excessive reactivity associated with high Pu concentrations and elevated melting temperatures.

To confirm the liquidus, solidus, and solid-phase transitions with greater accuracy - particularly the tentative transition line beyond 34.1 mol% CeF₃ - additional measurements exceeding 1000 °C and involving multiple heating-cooling cycles would be required to fully reach the single-phase liquid region. For instance, the three DSC peaks observed near 550 °C on the CeF₃-rich side of RbCeF₄ may represent localised compositions achieving the second eutectic melt due to incomplete melting, which would drive the residual solid composition further toward the CeF₃-rich region. X-ray diffraction analysis would also be beneficial to confirm the existence of intermediate compounds in the upper half of the phase diagram.

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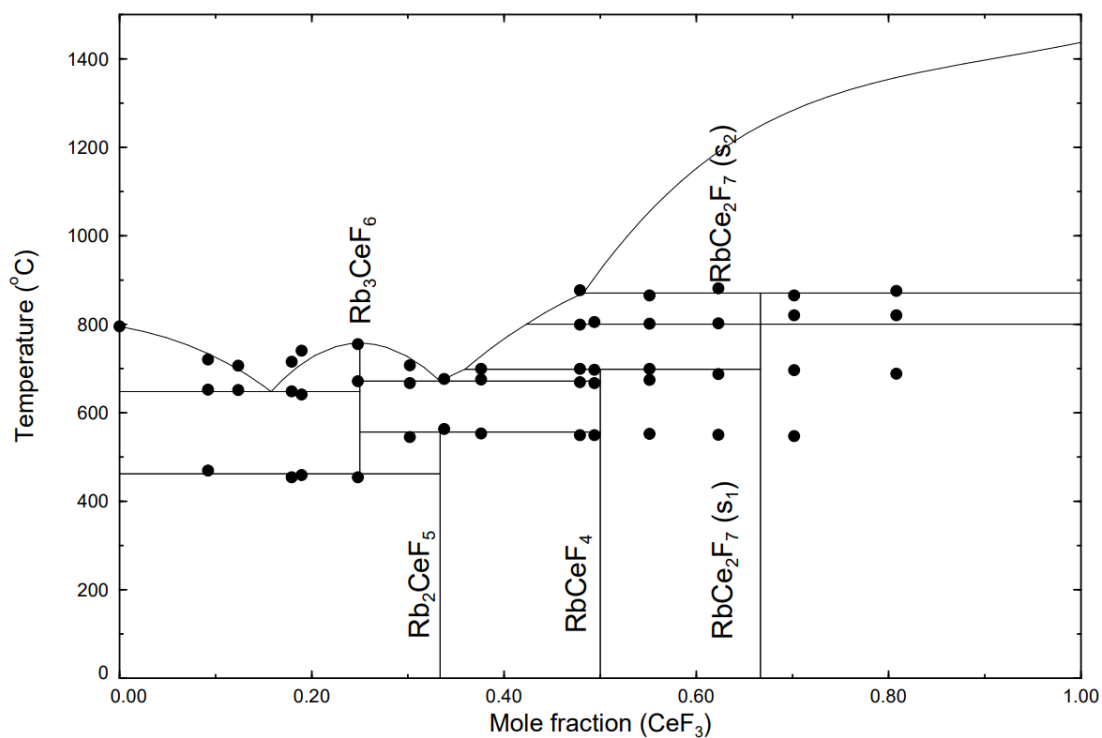


Fig. 4. 12: Comparison of the calculated RbF-CeF₃ phase diagram with the experimental DSC heating data points from (this work) ●.

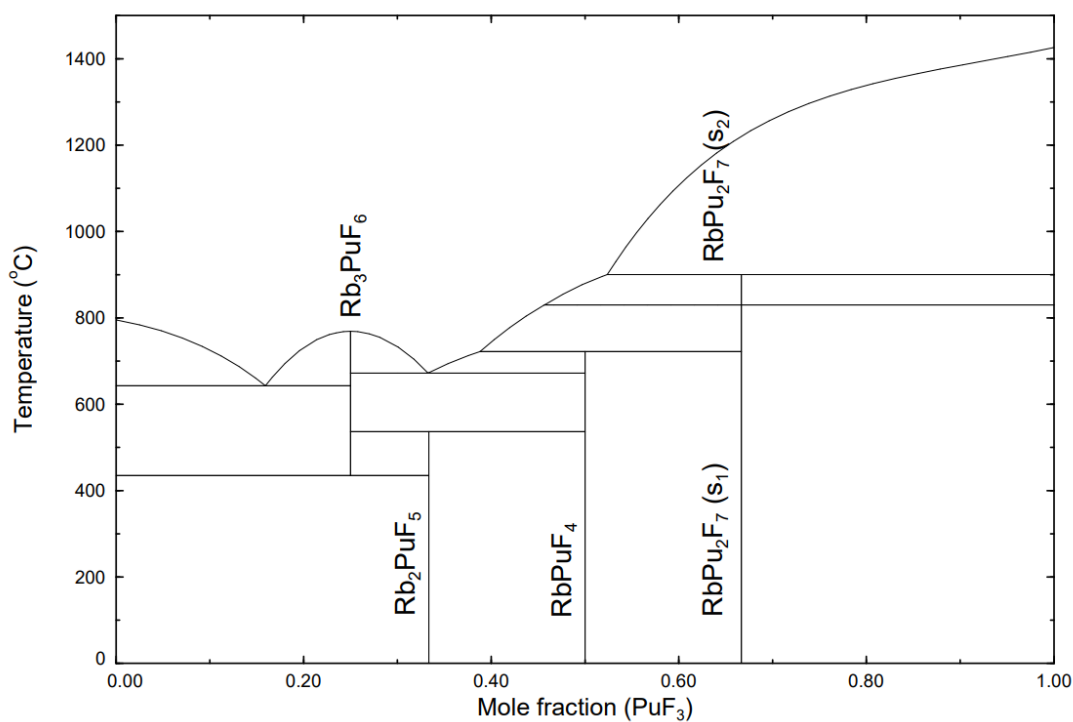


Fig. 4. 13: Calculated RbF-PuF₃ phase diagram (this work).

4.7.3 Calculated enthalpy of mixing

In the present study, a comparable ΔH_M value was independently calculated using the linear predictive method, with particular attention given to preserving the overall shape of the curve reported by Abdoun et al. (1997) [133], including the enthalpic minimum at $X(\text{MF}_3) = 0.4$. While this does not directly support the hypothesis of a distinct coordination complex $[\text{MF}_6]^{3-}$ with maximum short-range ordering at $X(\text{MF}_3) = 0.25$, to maintain charge-neutrality with three correspond Rb⁺ ions, recent work in molten FLiNaK has shown that $[\text{CeF}_6]^{3-}$ octahedra, influenced by surrounding alkali cations, are the predominant species, particularly in mixtures containing 42 mol% KF, with KF serving as a suitable surrogate for RbF (Cui et al. [114]). Until new Raman spectroscopy data become available, $[\text{CeF}_6]^{3-}$ will be assumed as the predominant species in this work. **Fig. 4.14** highlights the calculated enthalpy of mixing in this work:

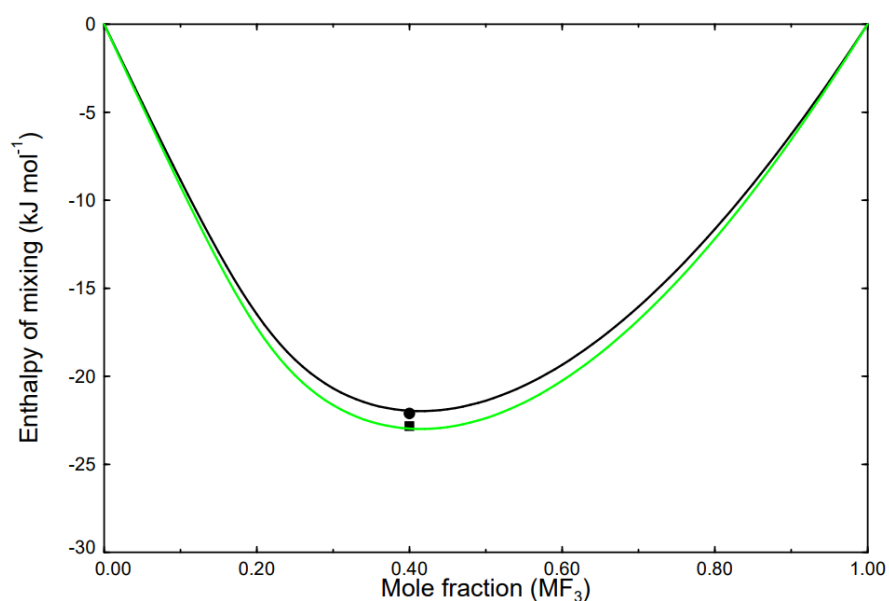


Fig. 4. 14: Calculated enthalpy of mixing of the RbF-MF₃ liquid solution, M = Ce (—), Pu (—). Temperature = 845°C, ● = Calculated RbF-CeF₃ minima by predicted linear method, ■ = Calculated RbF-PuF₃ minima by predicted linear method.

4.7.4 Liquid solution and excess properties

In this work, the liquid phase was modelled using the Modified Quasi-Chemical Model in the Quadruplet Approximation (MQMQA), which captures short-range

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ordering effects among both first-nearest neighbours (FNNs) and second-nearest neighbours (SNNs) by incorporating quadruplet interactions, as detailed in Section 4. This represents the first application of such an approach to the RbF-MF₃ systems (where M = Ce, Pu), incorporating the Gibbs energy function of one coordination complex within each melt at a composition of maximum short-range ordering at $X(\text{MF}_3) = 0.25$. This framework allows the six-coordinated metal fluoride complex to dominate in RbF-rich compositions, a trend further supported by the increased stability of the liquid phase observed in the phase diagram for compositions where $X(\text{MF}_3) < 0.4$.

In future studies involving different salt mixtures, the same cation may form alternative coordination environments beyond the six-coordinated complex. To ensure thermodynamic consistency, it will be necessary to apply minor corrections, introduced through manual iteration uniformly to the standard Gibbs energy expressions of all fluoride complexes. Careful documentation of these corrections will be essential to accurately assign each coordination species within varying chemical systems.

Table 4. 9: Optimised liquid solution parameters for RbF-CeF₃ liquid solution
Gibbs free energies in this work g^0 (J mol⁻¹).

$$\begin{aligned} \Delta g_{\text{RbCe}_{vi}/\text{F}_2} = & -25000 - (17100 + 0.8 \cdot (T/K)) \cdot \chi_{\text{Ce}_{vi}\text{Rb}/\text{F}_2} - 11200 \cdot \\ & \chi^2_{\text{Ce}_{vi}\text{Rb}/\text{F}_2} + 1.9 \cdot (T/K) \cdot \ln(T/K) \cdot \chi^3_{\text{Ce}_{iv}\text{Rb}/\text{F}_2} + 3 \cdot (T/K) \cdot \chi_{\text{RbCe}_{vi}/\text{F}_2} - 3.2 \cdot \\ & (T/K) \cdot \chi^2_{\text{RbCe}_{vi}/\text{F}_2} \end{aligned} \quad (15)$$

Table 4. 10: Optimised liquid solution parameters for RbF-PuF₃ liquid solution
Gibbs free energies in this work g^0 (J mol⁻¹).

$$\begin{aligned} \Delta g_{\text{RbPu}_{vi}/\text{F}_2} = & -26000 - 18100 \cdot \chi_{\text{Pu}_{vi}\text{Rb}/\text{F}_2} - 11800 \cdot \chi^2_{\text{Pu}_{vi}\text{Rb}/\text{F}_2} + 1.9 \cdot (T/K) \cdot \\ & \ln(T/K) \cdot \chi^3_{\text{Pu}_{iv}\text{Rb}/\text{F}_2} + 3 \cdot (T/K) \cdot \chi_{\text{RbPu}_{vi}/\text{F}_2} - 3.2 \cdot (T/K) \cdot \chi^2_{\text{RbPu}_{vi}/\text{F}_2} \end{aligned} \quad (16)$$

The parameters, along with the thermodynamic data for the solid Ce- and Rb-containing compounds provided in **Tables 4.9 & 4.10**, the phase diagrams shown

in **Fig. 4.12 & 4.13** was calculated. The two eutectic points of interest were successfully reproduced, showing strong agreement with the new experimental DSC results presented in this study. Additional DSC analysis will be necessary to more precisely establish the phase equilibria of the RbF-PuF₃ system. However, the present work is expected to offer improved insights compared to studies using the RbF-LaF₃ system as a surrogate.

The excess thermodynamic functions were calculated (**Fig. 4.15 & 4.16**) using the *FactSage software*. The resulting excess heat capacity and entropy show only minor deviations from ideal behaviour, similar to those observed in the LiF-UF₄ system reported by Ordaz-Flores et al.[103], but in contrast to the larger deviations described by ter Veer et al. (2025) [134] for other actinide-bearing salt systems. This briefly underscores that the choice of constituent salts can exert a significant influence on the resulting properties of molten salt mixtures. Consequently, greater attention should be given to salt selection, rather than assuming that all salts exhibit comparable behaviour. The activity (**Fig. 4.17**) of pure liquid CeF₃ and PuF₃ were calculated to demonstrated that RbF is highly effective in reducing their activities within the concentration ranges of a suitable MSR fuel choices.

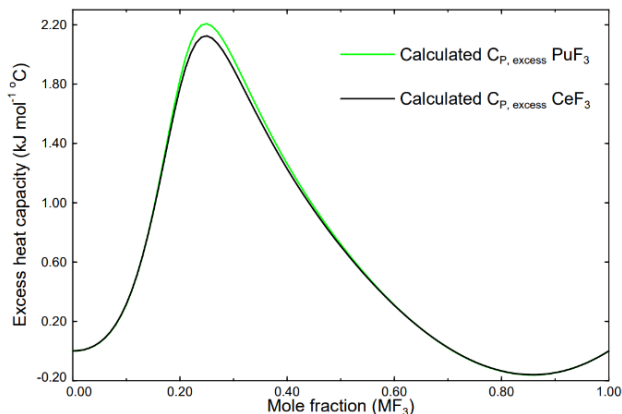


Fig. 4. 15: Calculated excess heat capacity of the liquid solution as a function of MF₃ composition, M = Ce, Pu; T = 700°C.

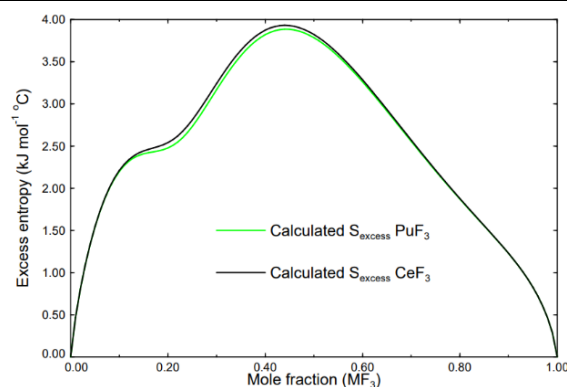


Fig. 4. 16: Calculated excess entropy of the liquid solution as a function of MF₃ composition, M = Ce, Pu; T = 850°C.

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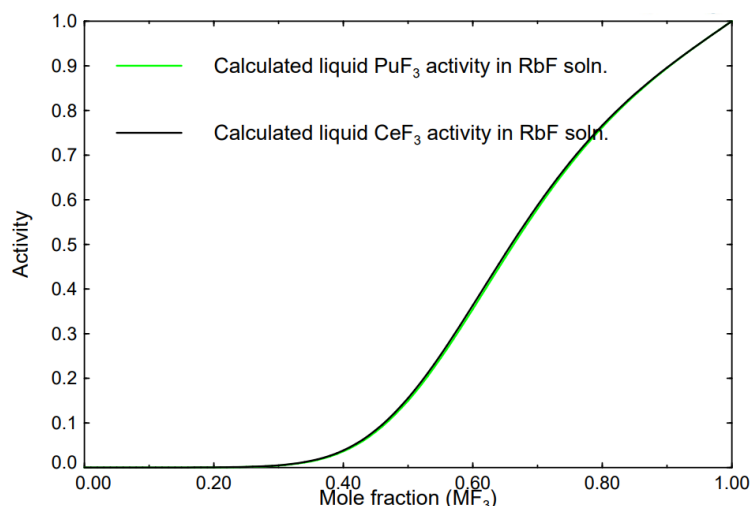


Fig. 4. 17: Calculated chemical activity of liquid MF₃, M = Ce, Pu, in RbF solution, T = 850 °C.

4.7.5 Redox control and corrosion mitigation

The transport of corrosion products in molten salt reactors (MSRs) is governed by gradients in Gibbs free energy, primarily driven by thermally induced differences in chemical potential [75]. As such, a robust thermodynamic framework is critical for accurately representing the fundamental forces that drive corrosion processes, necessitating the incorporation of rigorously defined thermodynamic models within multiphysics reactor simulation tools. In the MSRE, researchers at ORNL identified control of the redox potential as a key strategy for mitigating alloy corrosion in molten fuel salts [78]. High-nickel alloys, such as Hastelloy-N, were developed to replace stainless steels, which were susceptible to selective leaching of alloying elements like chromium, resulting in the formation of chromium fluoride species in the salt. Chromium, a critical element for the formation of protective Cr₂O₃ surface layers, was observed to be depleted from alloy surfaces and found in elevated concentrations within the salt. To counteract this, the redox potential of the LiF-BeF₂-ZrF₄-UF₄ fuel salt was deliberately lowered through the addition of U³⁺, altering the U⁴⁺/U³⁺ ratio, thereby creating a more reducing environment, an approach demonstrated to effectively suppress corrosion.

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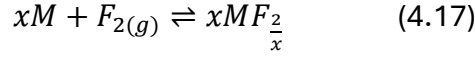
A thermodynamic assessment of the original MSRE fuel system (LiF-BeF₂-ZrF₄-UF₄) was previously conducted by Beneš et al. (2008) [135]. When their thermodynamic data were implemented in *FactSage* 8.3, the calculated enthalpy of mixing for several sub-binary systems showed significantly non-zero values near the end members, which is thermodynamically inconsistent. Consequently, Beneš' dataset was not adopted in this work, as it would have produced unreliable thermodynamic results. Instead, the reassessment by Capelli et al. (2015) [136] was used, as it provided a more internally consistent description of the LiF-BeF₂-UF₄ system. As illustrated in **Fig. 4.18**, the thermodynamic evaluations from Capelli et al. [25] for the two ternary eutectics in the LiF-BeF₂-UF₄ system are plotted alongside the RbF-PuF₃ system developed in this study. The LiF-BeF₂-UF₄ eutectics indeed exhibit a higher redox potential, indicating a more oxidising nature due to their less negative total Gibbs energies. Notably, the second ternary eutectic, LiF-BeF₂-UF₄ (2), is only marginally more reducing than pure UF₄ - the most oxidising constituent of a typical MSR start-up fuel mixture.

Plutonium tetrafluoride (PuF₄) is generally recognised as thermodynamically stable, unlike its chloride analogue, PuCl₄ [79][137], but it may also play a role in redox control through adjustment of the Pu⁴⁺/Pu³⁺ ratio. Notably, PuF₃ represents a viable initial fissile component for molten salt fast reactors (MSFRs), offering an alternative to the down-blending or geological disposal of the UK's existing Pu stockpile[138]. Moreover, PuF₃ is anticipated to form in situ via neutron capture by ²³⁸U during reactor operation.

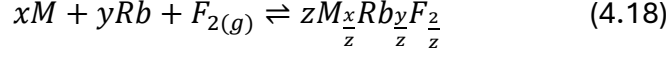
However, the potential impact of base salt additions, such as AF (where A = Li, Na, K, Rb), on the redox potential of the system is often overlooked. In this work, we demonstrate that even without altering the Pu⁴⁺/Pu³⁺ ratio, the incorporation of RbF can yield beneficial effects by lowering the Gibbs free energy of the system, effectively rendering the salt more reducing.

One method to illustrate how the Gibbs free energy change of reactions between the alloying components and various salts versus temperature is through use of an Ellingham diagram. The Gibbs free energy change of these formation reactions per mol of F₂ (g) can be simplified as:

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Where x is the stoichiometric coefficient to balance the reaction per mole of pure F₂ gas, M is metal element (M = Mo, Ni, Fe, Cr, Mn, U, Pu, Rb). Or in the case of the formation of the molten salt solution in this work:



Where y and z are additional stoichiometric coefficients to balance the reaction per mole of pure F₂ gas for the RbF-PuF₃ solution.

The Gibbs free energy of the forward reaction per mole of F₂(g) in Equation 4.25 can then be written as:

$$\Delta G_r^\circ = xG_{MF_{\frac{2}{x}}}^\circ - \left(xG_M^\circ + xG_{F_{2(g)}}^\circ \right) \quad (4.19)$$

Similarly for equation 26, the Gibbs free energy of the forward reaction per mole of F₂(g) for the RbF-PuF₃ solution:

$$\Delta G_r^\circ = zG_{M_{\frac{x}{z}}Rb_{\frac{y}{z}}F_{\frac{2}{z}}}^\circ - \left(xG_M^\circ + yG_Rb^\circ + xG_{F_{2(g)}}^\circ \right) \quad (4.20)$$

Here, in this work, the newly modelled RbF-PuF₃ system, two eutectics at composition X(PuF₃) = 0.16, 0.33, where both potentials are plotted against other pure salts components including alloy corrosion products in **Fig. 4.18**:

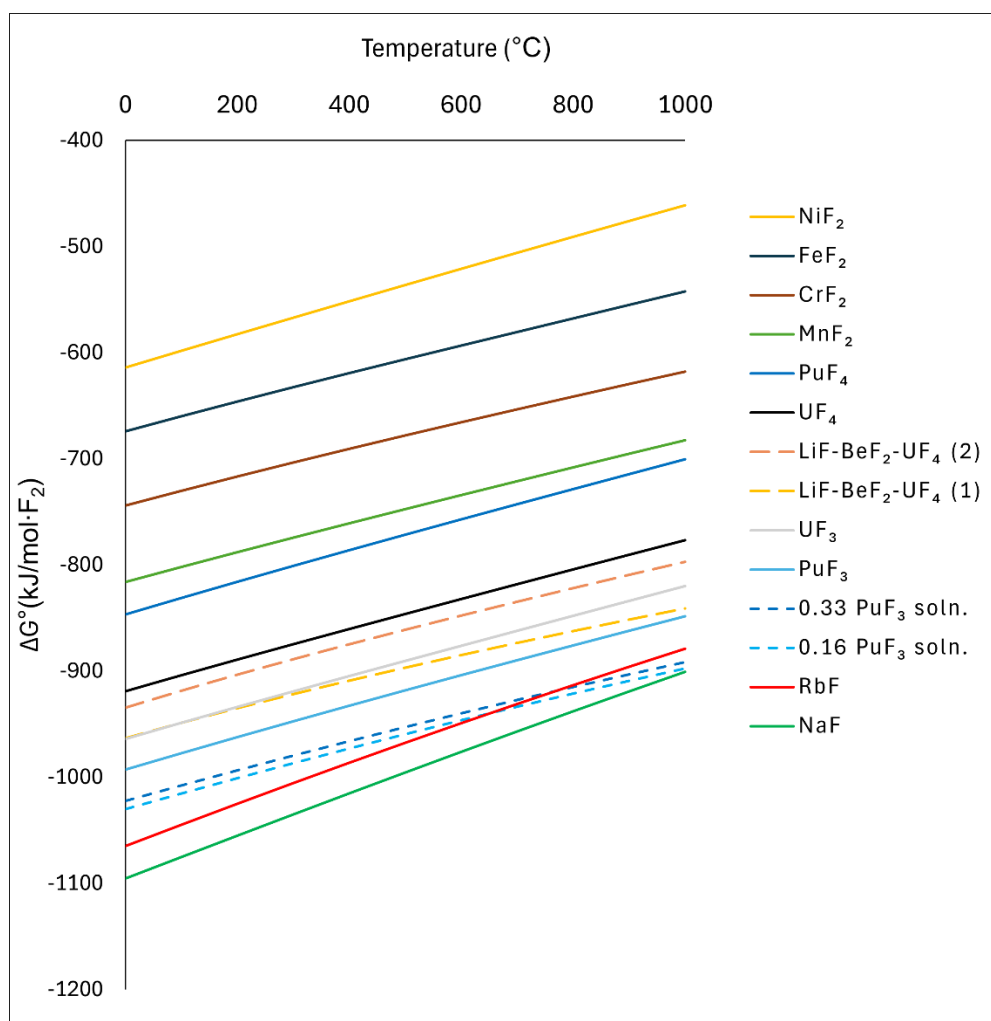


Fig. 4. 18: Standard Gibbs free energy of formation per mole of F₂ for salt components, corrosion products and molten salt solution (RbF-PuF₃ soln.) of the binary molten salt modelled in this work at composition $X(\text{PuF}_3) = 0.16, 0.33$. Other data from Gurvich [68].

Previous work at ORNL during the Aircraft Reactor Experiment (ARE) [80] and more recent review by Kairos in collaboration with Argonne National Laboratory [81] highlighted the importance of cation–anion size effects, particularly through the charge-to-radius (Z/r) ratio. Deviations from ideal solution behaviour often arise from negative heats of mixing, where the mixed salt is energetically more stable than its pure components, and from positive excess entropies due to increased lattice disorder when dissimilar cations are combined.

For example, in NaF-ZrF₄ mixtures, the addition of UF₄ decreased ZrF₄ activity but simultaneously destabilised UF₄ compared with AlkF mixtures without ZrF₄. Interestingly, the reduction in ZrF₄ activity was less pronounced than the effect on

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UF₄ stability. This behaviour supports the idea that molten salt thermodynamics are strongly influenced by Z/r ratios. Flexible molten lattices tend to adopt cation arrangements that minimise energy, increasing electrostatic attraction and lattice distortion, commonly, but not universally, enhances disorder. This can explain why activity coefficients are often far below one and why more negative enthalpies of mixing are observed in heavier AlkF series (demonstrated in **Fig. 4.6**).

However, differences in Z/r alone cannot explain all non-ideal behaviours. ORNL attributed further deviations to complex formation within the melt, particularly when fluorine-rich components such as UF₄ are present. These thermodynamic models only incorporate one complex, such as [MF₆]³⁻ which dominate at one MF₃ concentration. Complexation can contribute substantially to non-ideal behaviour, especially in systems with both charge and size disparities (e.g., NaF-ZrF₄ and RbF-PuF₃). Experimental evidence, such as the KF-ZrF₄ system studied by Sun (2019), has refined earlier hypotheses on fluoride bridging and coordination environments.

ORNL [80] also described these systems in terms of “fluoroacidity.” In NaF-ZrF₄, Na⁺ acts as the fluoride donor (basic) and Zr⁴⁺ as the fluoride acceptor (acidic). Analogously, in RbF-MF₃, Rb⁺ donates fluoride while M³⁺ accepts it, leading to complexes such [MF₆]³⁻. The stronger acid-base interaction in this system produces greater negative deviations from ideal solution behaviour. Rb’s high basicity promotes fluoride donation to Ce and Pu, stabilising the melt and reducing the dissolution of alloying elements.

Figure 2.3.2 of the ORNL report [80] illustrates the acid-base scale for fluoride salts, showing that RbF is more basic than LiF. Such comparisons help predict solubility and non-ideal deviations, which in turn inform solvent selection for corrosion mitigation. The results suggest that while RbF-PuF₃ mixtures may have different eutectic melting points and even higher PuF₃ concentration than LiF-PuF₃ or NaF-PuF₃, they may offer better corrosion resistance for structural alloys. This is attributed to RbF’s stronger ability to stabilise actinide complexes rather than facilitating alloy dissolution.

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The use of RbF as a solvent component, appears to significantly lower the redox potential of the salt system. Molten LiF-BeF₂-ThF₄ salt, was shown to effectively mitigate chromium dissolution and tellurium-induced cracking, with UF₃ additions [77] [76]. Since UF₃ is the predominant source of uranium carbide formation in molten fluoride systems [23], this finding is particularly relevant for reactor materials compatibility. By reducing the chemical activity of actinide fluorides such as UF₃ or PuF₃, RbF not only lowers the redox potential but also suppresses undesirable side reactions that compromise structural integrity. Consequently, the incorporation of RbF may represent a promising approach for enhancing both the chemical and thermodynamic stability of MSR fuel salts.

These findings align with more recent studies, such as Ocádiz Flores et al. (2021) [82], which emphasize that lowering the Gibbs free energy of molten salt systems enhances thermodynamic stability. Other studies have highlighted the role of impurities in corrosion behaviour, underscoring the need for further experimental validation. Finally, although heavier alkali fluorides may enhance corrosion resistance, further experimental investigation is warranted to substantiate and validate this promising hypothesis and its potential applicability to molten salt systems.

4.8 Conclusion

The RbF-PuF₃ system is a key binary for assessing RbF-containing Pu- and U-based salts in MSRs, as ²³⁸U transmutes to ²³⁹Pu and ²⁴⁰Pu under neutron irradiation. In this work, the system is experimentally investigated using CeF₃ as a surrogate and thermodynamically modelled. This work accounts for six-coordinated Pu complexes in the melt, like to those identified in Ce systems via Raman spectroscopy. This species exhibits distinct short-range ordering behaviours at one set composition, representing a novel advancement in the thermodynamic characterisation of fluoride fuel salts. Furthermore, the results presented here, pending further experimental validation, suggest that CeF₃ may represent the most

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suitable surrogate for PuF₃ to date, offering improved compatibility compared to previously studied LaF₃.

The RbF-PuF₃ system presents several potential advantages among the other alkali fluoride binary systems, notably the anticipated existence of two moderate-temperature eutectics at compositions $X(\text{PuF}_3) = 0.15$ (642°C) and $X(\text{PuF}_3) = 0.33$ (671°C). Although the LiF-PuF₃ and NaF-PuF₃ systems exhibit relatively simple binary phase diagrams, each containing a single eutectic point, these eutectics occur at higher temperatures - 739°C at $X(\text{PuF}_3) = 0.21$ for LiF and 727°C at $X(\text{PuF}_3) = 0.25$ for NaF. In contrast, the lower eutectic temperature and higher PuF₃ solubility observed in the RbF-PuF₃ system indicate that RbF may provide a more favourable solvent environment for MSR fuel applications. The KF-PuF₃ system remains experimentally unexplored, including its surrogate KF-CeF₃ system, may represent a potentially meaningful area for future research. CsF, also unexplored, its mono-isotopic nature (¹³³Cs), exhibits prohibitively large neutron absorption cross sections (29 ± 1 b), resulting in the production of the radiologically significant isotope ¹³⁴Cs. This renders CsF unsuitable for use as a carrier salt in fuel mixtures. In contrast, Rb exists as two naturally occurring isotopes, ⁸⁵Rb and ⁸⁷Rb, with comparatively low neutron absorption cross sections (0.48 ± 0.01 b and 0.12 ± 0.03 b respectively [86]), none of which give rise to safety-relevant isotopes.

The projected second eutectic at $X(\text{PuF}_3) = 0.33$ may permit greater Pu loading compared not only to the first eutectic in RbF at $X(\text{PuF}_3) = 0.15$, but also to the eutectics in LiF and NaF systems. This increased loading capacity could support the development of smaller, more compact MSR cores, potentially reducing the size of critical core components and contributing to lower capital costs. This could be an alternative strategy for use of the 140 tonnes of Pu stored at Sellafield in the UK [138], instead of down blending, vitrifying followed by final deep geological repository storage. The isotopic makeup of this Pu at Sellafield is unknown, the first eutectic with less Pu loading could be more beneficial to limit fission reactivity if the isotopic content of fissile ²³⁹Pu is too high.

Accordingly, RbF emerges as a possible candidate for use in advanced fluoride-based fuel salt systems. The UF₃/UF₄ ratio is often discussed in the literature as a

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means of controlling redox potential and reducing corrosion in structural alloys. However, limited attention has been devoted to comparing the redox potentials of different thermodynamically characterised actinide salt solutions, their compositional variations, and their capacity to form complexes that may exhibit greater thermodynamic stability, thereby reducing the dissolution rates of alloying components. This work addresses that gap by examining their relevance to corrosion behaviour using *Factsage software* and Ellingham diagram.

This study underscores the importance of robust methods for determining thermodynamic properties in data-scarce systems. By improving DSC sensitivity with low-mass crucibles and extending Gibbs energy functions to include multi-coordinated Pu and Ce complexes, it provides an efficient framework for modelling with minimal sample use and reduced waste. As a binary salt system study, these findings provide a critical foundation for future investigations into ternary and higher-order actinide-containing salts, supporting the development of advanced fuel cycles and next-generation molten salt reactor (MSR) technologies.

4.9 Acknowledgements

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Chapter 5: Thermodynamics of the RbF-UF₄ system: a potential fuel candidate for molten salt reactors

Joshua Findlay¹, Patrice Chartrand², David Cheneler¹, David Leblanc³, Claude Degueldre¹

1. School of Engineering, Lancaster University, Lancaster LA1 4YW UK
2. Department of chemical engineering, Polytechnique Montreal, Montreal, H3C 3A7, Canada
3. Terrestrial Energy Ontario Inc., 2275 Upper Middle Rd., Oakville, ON L6H 0C3, Canada

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5.1 Abstract

Thermodynamic properties of the RbF-UF₄ system, a potential fuel for Molten Salt Reactors (MSR), have been investigated for the first time combining experimental data gained by Differential Scanning Calorimetry (DSC), comparing literature data with those obtained by modelling. A comprehensive understanding of phase changes across various compositions and temperatures is presented together with the enthalpy and entropy related parameters of the considered phases. This study underscores the importance of the purity of compounds and the equilibrium between coexisting phases. The use of performant custom-designed light-weight crucibles provides reliable phase equilibria data and phase diagram reconstruction. In addition to the transformation enthalpies, heat capacities from solid to liquid transitions are measured for the most relevant compositions of the MSR fuel e.g. eutectic. In the absence of complete experimental data for intermediate compounds, the study explores the potential of estimating the heat capacities of individual compounds using Neumann-Kopp approach as a pragmatic way to describe the properties of the system. Emphasis is placed on the role of Rb_mU_nF_{4n+m} solid complexes that play a relevant role on phase properties during phase transitions and three eutectics, offering a higher actinide solubility and a more thermodynamically stable fuel than the more commonly explored singular eutectic LiF-UF₄ and NaF-UF₄ systems. The newly optimised RbF-UF₄ liquid solution

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has also been analysed in an Ellingham diagram with other common fluoride salts and alloy components to compare the redox potential that may improve corrosion resistance.

Keywords: RbF-UF₄ system; Differential Scanning Calorimetry; Phase diagram; Heat capacity; Molten salt reactor fuel

Corresponding author: j.findlay1@lancaster.ac.uk

5.2 Introduction

In the 1950's and 60's, in the U.S. at Oak Ridge National Laboratory (ORNL), the Molten Salt Reactor (MSR) emerged as an alternative nuclear technology in the to the more extensively tested and established Pressurised Water Reactor (PWR) system. Molten salt reactor (MSR) technology has recently re-emerged as a promising alternative to PWR systems, providing notable advantages while still facing challenges to commercialisation (Bostelmann et al., 2022). [89]. These reactors, characterized using liquid salts as both fuel and coolant, offer advantages in terms of safety, fuel utilisation efficiency, and waste production reduction compared to more traditional solid-fuel water cooled nuclear reactor designs.

The primary challenge posed by MSRs is the utilization of liquid fuel during operation, which is significantly different, in terms of operation, refuelling and corrosion from solid fuel in other reactor technologies as reported by Merle-Lucotte et al. (2008) [110]. The entire reactor is constructed around this uranium-based salt dissolved in other molten salts, which introduces lower melting points of a pure salt, and many other different neutronic, physical and chemical properties than using a pure uranium salt by itself, e.g. UF₄ or UCl₃. Notably, the molten salt mixture serves dual roles: as fuel and as a heat exchanger fluid, see for example Uhlíř (2007) [139].

The less-studied RbF-containing system was investigated at Lancaster University in the context of molten salt reactors. Although D. F. Williams et al. (2006) [140] identified RbF in other fluoride systems as a potential reciprocal component for

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MSR fuels, this work focuses specifically on the RbF-UF₄ binary as a direct fuel mixture. This consideration is based on the neutronic properties of rubidium, specifically, the low neutron absorption cross-section of its two isotopes and the short half-lives of its radioactive daughter isotopes [111]. Historically, several non-water-cooled reactors have utilised liquid metals such as sodium or sodium-potassium alloy as coolants, due to their favourable neutronic and thermophysical characteristics. Although rubidium shares chemical similarities with sodium and potassium, it was quickly dismissed as a coolant candidate in its metallic form due to its high vapour pressure. However, this paper explores the potential of using rubidium in the form of a fluoride salt within a reactor core configuration. In this form, rubidium exhibits drastically different physico-chemical properties while retaining the same advantageous neutronic characteristics.

It is well-established that UF₄ binary systems with heavier alkali metal fluorides such as KF, RbF, and CsF exhibit comparable phase diagrams and intermediate compounds. As reported by Schacherl et al. (2021) [104] and others [141], these systems display similar features, including the formation of solid intermediate compounds, consistent liquidus slopes, and comparable enthalpies of phase transitions (ΔH_{tr}). These thermodynamic properties are critical to the performance and efficiency of molten salt reactors (MSRs).

This study focuses on the RbF-UF₄ system, which, despite its potential, has received less attention compared to lighter alkali systems, particularly LiF-UF₄. LiF is widely studied due to its attractive, simple singular low-temperature eutectic at 750 K with $X(\text{UF}_4) = 0.27$, as reported by Ocadiz-Flores (2021) [103]. However, the use of LiF comes with significant challenges. Natural lithium consists of two isotopes, ⁶Li and ⁷Li; the latter has a high neutron absorption cross-section and undergoes fission, producing tritium, a problematic radioisotope in nuclear power systems. Isotopic separation of ⁷Li is therefore necessary to reduce tritium generation, but even with enriched ⁷Li, residual ⁶Li can still lead to unwanted tritium production.

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Heavier alkali fluorides such as RbF offer a potential alternative that avoids these issues entirely, as rubidium does not require isotopic purification and does not contribute to tritium generation. In contrast to the LiF-UF₄ system, which features a single eutectic at low UF₄ content ($X = 0.27$), binary systems with heavier alkali fluorides, such as NaF-UF₄, KF-UF₄, RbF-UF₄, and CsF-UF₄ exhibit multiple eutectics at higher UF₄ concentrations, though at elevated temperatures exceeding 750 K. While CsF is excluded from consideration as a beginning-of-life (BOG) fuel salt component due to its poor neutronic performance, the strong tendency of formation of CsF from ¹³⁷Cs (another problematic fission product) means the CsF-UF₄ binary system remains relevant for future thermodynamic models that incorporate fission product behaviour. Therefore, the use of NaF, KF, and RbF enables the formulation of fuel salts with higher fissile MF₄ (M = U, Pu) loading. Although their binary eutectics have unfavourable higher melting points beyond 750 K, ternary and higher-order systems incorporating these heavier alkali fluorides may accommodate increased actinide loading while preserving the low melting characteristics associated with the LiF-UF₄ binary system. This combination could enhance neutron economy and burnup, offering potential for more compact and economically efficient MSR designs. While RbF-UF₄ itself may represent a promising candidate fuel salt, the thermodynamic modelling and analysis presented in this work also serve as a critical foundation for developing more complex salt systems that include fission products and additional fluoride components.

This work contributes to the assessment of the RbF-UF₄ binary phase diagram and the thermodynamic properties of all phases and compounds within it. It presents new phase equilibria data from Differential Scanning Calorimetry (DSC), producing heat derived parameters from experiments and results produced using Factsage software (version 8.3) computational modelling utilising the modified quasi-chemical model which, incorporates Gibbs free energy exchange of the degree ‘short-range ordering’ of the various ions and complexes within the molten mixture due to their differences in ionic charges and radii. For the first time, the liquid phase has been modelled to include the complex species [UF₇]³⁻, [UF₆]²⁻, and [UF₅]⁻. The selection of [UF₇]³⁻, [UF₆]²⁻, and [UF₅]⁻ complexes in this study is informed by the work

of Sun et al. (2019) [142], who reported analogous [ZrF₇]³⁻, [ZrF₆]²⁻, and [ZrF₅]⁻ species in the KF-ZrF₄ (58–42 mol %) melt. Since ZrF₄ serves as a robust structural and thermodynamic surrogate for UF₄, and KF closely mimics the properties of RbF, the coordination behaviour observed in the zirconium system provides a strong basis for adopting these uranium–fluoride species in our model. When applied to binary systems, this method establishes a robust foundation for constructing higher-order systems (e.g., ternary, quaternary), ensuring accurate thermodynamic predictions as the complexity of the fuel salt increases with the accumulation of fission products.

5.3 Background and literature data

5.3.1 Phase diagram insights and prior investigations

The choice of fuel salt components and proportions must meet multiple operational and neutronic criteria: melting point compatible with the reactor's minimum operating temperature, sufficient density and heat capacity, low viscosity for reliable flow, and compliance with fissile-enrichment limits. Reported binary phase behaviour varies by alkali fluoride: LiF-MF₄ (M = Th, U) shows a single, low-temperature eutectic [103], [101], while NaF-UF₄ and KF-UF₄ each exhibit multiple eutectics [143]. Larger-X(MF₄) eutectics can be advantageous for neutron economy but occur at elevated temperatures that may limit practical application. In this work, RbF-UF₄ shows phase behaviour similar to KF-UF₄; by incorporating complexes identified via Raman spectroscopy into the thermodynamic model, we improve predictive accuracy for ternary and higher-order systems. Finally, thermal-analysis data for RbF-UF₄ system is decades-old and merit re-evaluation. CsF is not considered further here because of its unfavourable neutronic properties. Experimental validation is required to confirm any proposed salt formulations and their impact on neutron economy and fuel burnup.

Two prior experimental examinations have been conducted on the RbF-UF₄ binary phase diagram by Freidman et al. (1956) [144] and by Thoma et al. (1958) [145] at ORNL (Oak Ridge National Laboratory). Both exhibit slight variations in phase

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diagram determination as shown below in **Fig. 5.1 & 5.2**. In both reports, two methods of phase equilibria were made; thermal analysis and quenching combined with optical microscopy and XRD (X-Ray Diffraction). The processes are described in detail by the report by Barton et al. (1958) [146] and discussed in more detail later in this work.

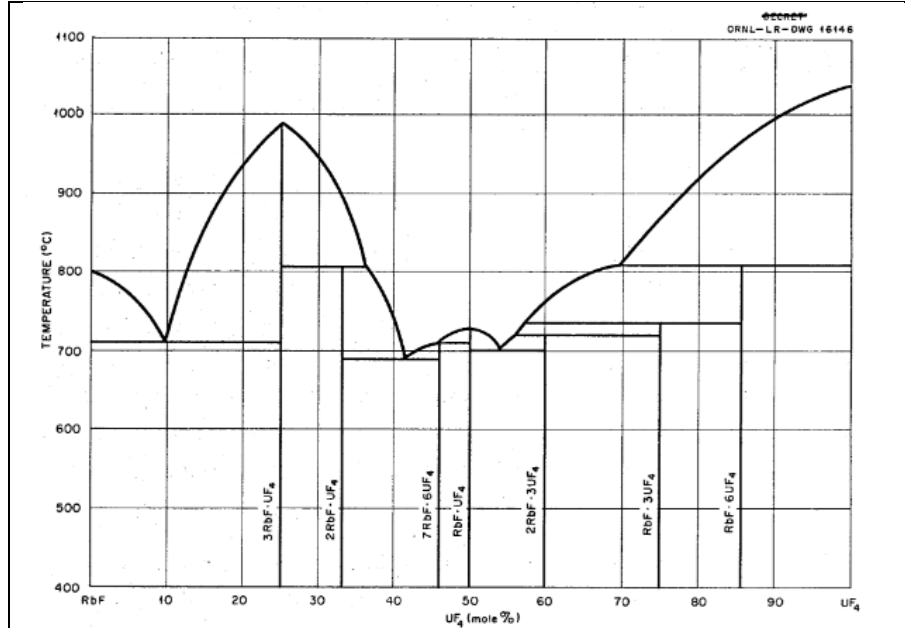


Fig. 5. 1: RbF-UF₄ phase diagram determined by Friedman et al. (1956) [144] (with permission from Elsevier).

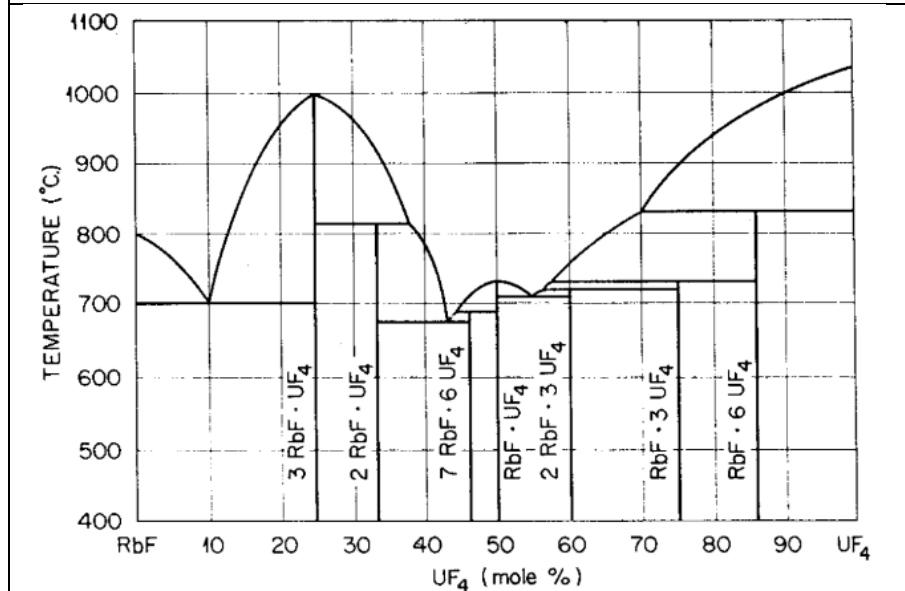


Fig. 5. 2: RbF-UF₄ phase diagram determined by Thoma et al. (1958) [145] (with permission from Elsevier).

5.3.2 Crystallographic data

The crystallographic data of compounds are essential for understanding their structural and physical properties. These data provide insights into the atomic arrangement, space groups, and lattice parameters, which are essential for phase diagram assessments. Nevertheless, it remains important to document these structures, as the future development of higher-order systems incorporating RbF-MF₄ (M = Zr, Th, U) binary components may lead to the formation of intermediate compounds exhibiting similar crystal structures. In such scenarios, depending on the composition and temperature, the presence of structurally compatible phases could enable interstitial cation substitution within a common sublattice, rather than leading to the formation of multiple distinct solid phases. For example, instead of Rb₂UF₆ and K₂UF₆ of shared crystallography coexisting within the same phase field of the ternary KF-RbF-UF₄ system, a continuous solid solution of the type Rb_xK_{2-x}UF₆ ($0 \leq x \leq 2$) may form, exhibiting a uniform crystallographic structure and phase type. In this study two end member compounds (RbF and UF₄) and seven intermediate compounds within the UF₄-RbF binary system; Rb₃UF₇, Rb₂UF₆, Rb₇U₆F₃₁, RbUF₅, Rb₂U₃F₁₄, RbU₃F₁₃ and RbU₆F₂₅ are reported in literature. **Table 5.1** summarizes the data from the end members and complexes investigated.

Table 5. 1: Crystallographic data of rubidium fluoride and uranium tetrafluoride compounds from literature.

Fluoride	RbF mol%	<i>M</i> g mol ⁻¹	Space group	ρ g cm ⁻³	Ref.
RbF	100.00	104.466	<i>Fm</i> $\bar{3}m^*$ <i>Pm</i> $\bar{3}m$	3.67 4.53	D'ans & Lax (1997) [123]
Rb ₃ UF ₇	75.00	627.422	<i>cF</i> 520	4.74	Springer materials [147] and Harris (1958) [148]
Rb ₂ UF ₆	66.67	522.955	<i>Cmcm</i>	5.20	Kruse (1971) [149]
Rb ₇ U ₆ F ₃₁	53.84	2017.123	<i>P</i> 6 ₃	6.02	Thoma <i>et al</i> (1958) [145]
RbUF ₅	50.00	418.489	<i>P</i> 2 ₁ / <i>c</i>	6.12	Yeon <i>et al</i> (2014) [150]
RbU ₃ F ₁₃	25.00	1046.534	<i>Pmc</i> 2 ₁	7.013	Yeon <i>et al</i> (2014) [150]
RbU ₆ F ₂₅	20.00	1988.601	<i>P</i> 6 ₃	6.91	Mighell <i>et al</i> (1977) [151]
UF ₄	0.00	314.023	<i>mS</i> 60 or <i>C</i> 12/ <i>c</i> 1	6.71	Kern <i>et al</i> (1994) [152]

5.3.3 Estimation of Enthalpy of Mixing from Literature Data

The accuracy of binary molten salt models can be enhanced by incorporating experimental enthalpy of mixing data into the Gibbs energy's parameters within the Factsage software. In the absence of sufficient experimental data, previous authors rely on empirical interpolation and extrapolation methods to estimate values from available data on related salt systems, using ionic radii parameters as a basis, an approach first recognised by Davis *et al.* (1964) [128]. This was improved upon by Østvold (1971) [153] and implemented by many subsequent authors later discussed in this work, given by Eq. 5.1 - the δ_{12} parameter is defined as:

$$\delta_{12} = \frac{[r_A^+ + r_X^-] - [r_M^{4+} + r_X^-]}{[r_A^+ + r_X^-][r_M^{4+} + r_X^-]} \quad (5.11)$$

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Where r_A^+ is the ionic radius of the alkali metal cation, r_M^{4+} is the ionic radii of the tetravalent metal cation (M = Zr, Th, U) and r_X^- is the ionic radii of fluorine or chloride in each binary system taken from R.D. Shannon (1976) [107].

No experimental data for the RbF-UF₄ system exists for the enthalpy of mixing, neither do many for AlkF-UF₄ (where Alk = Na, K, Rb, Cs) or RbF-MF₄ (where M = tetravalent metallic cation) mixtures. Therefore, the linear prediction method as a function of ionic radii parameter, δ_{12} - used by Robeline et al. (2011) [55], or the correlation approach by Schorne-Pinto (2021) [58] could not be used for calculation.

Experimental data exists for Alk-ZrF₄ mixtures by Hatem et al. (1989) [100], for LiF-ThF₄ by Capelli et al. (2013) [101], NaF-ThF₄ by Schreuder et al. (2021) [102] and LiF-UF₄ by Ocadiz-Flores et al. (2021) [103]. All other enthalpy of mixing data presented here is calculated, shown below by **Fig. 5.3** for the Alk-ThF₄, Alk-UF₄ and Alk-ZrF₄ systems. As KF-UF₄ and Cs-UF₄ systems have already been calculated [104], as expressed in their Gibbs energy functions presented in their separate papers/report, the RbF-UF₄ value system shown in **Fig. 5.3** was interpolated between the two.

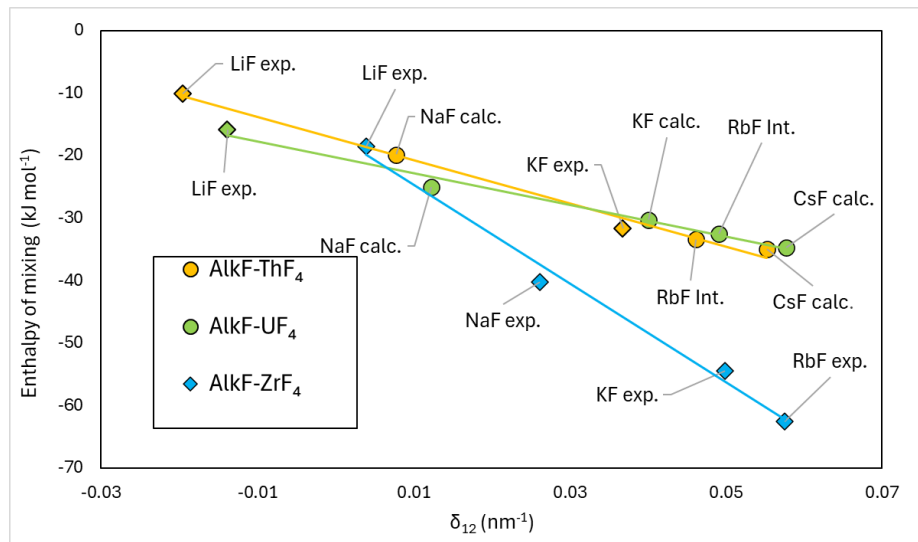


Fig. 5. 3: Experimental and calculated minimum enthalpy of mixing data of AlkF-MF₄ systems (where M = Zr, U, Th; Alk = Li, Na, K, Rb) and δ_{12} as defined in Equation 4.9. The blue plot is the entire AlkF – ZrF₄ series by Hatem et al. (1989) [100] exp., the orange plot contains separate data for the AlkF-ThF₄ series, LiF-ThF₄ by Capelli et al. (2013) [101] exp., NaF-ThF₄ by Schreuder et al. (2021) [102] calc., KF-ThF₄ by Ocadiz-

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Flores et al. (2020) [143] exp., LiF-UF₄ by Ocadiz-Flores et al. (2021) [103] exp., NaF-UF₄ and KF-UF₄ by Schacherl et al. (2021) [104] calc., and RbF-UF₄ (this work), CsF-UF₄ calc. by Xiang et al. (2017) [141].

While the calculated values provide useful estimates, they cannot be fully relied upon due to the assumptions involved in their derivation. In contrast, experimental values offer greater reliability, as they are derived from direct measurement. As noted by Østvold [153] and later by Schorne-Pinto et al. [58], for a given composition, the enthalpy of mixing within a series of alkali–metal halides exhibit an approximately linear relationship with the δ_{12} parameter. As δ_{12} is a function of the ionic radii of three species in a halide binary system, in this case, Alk⁺ (Alk = Li, Na, K, Rb, Cs), M⁴⁺ (M = Zr, U, Th) and F⁻.

In this work, the enthalpy of mixing for the AlkF-UF₄ system is calculated to be more negative than the values presented in **Fig. 5.3**. The effective ionic radius of U⁴⁺ (0.089 nm) lies approximately midway between that of Th⁴⁺ (0.094 nm) and Zr⁴⁺ (0.072 nm). A comparable trend is observed in the AlkCl-LnCl₃ and AlkF-LnF₃ systems, where linear gradients do not reveal a consistent pattern; instead, analysing the relative increases in enthalpy of mixing between successive alkali chlorides (e.g., Li to Na, Na to K) provides a more reliable descriptor. For instance, in the Ln³⁺ chloride series, La³⁺, with the largest ionic radius (0.1032 nm), and Tm³⁺, one of the smallest (0.0880 nm), define two distinct sets of relative enthalpy increases across the alkali chloride series. When examining lanthanides with intermediate ionic radii, such as Tb³⁺ (0.0923 nm), the relative enthalpy increases for AlkCl-TbCl₃ mixtures fall between those of the AlkCl-LaCl₃ and AlkCl-TmCl₃ systems, supporting the correlation between ionic radius and the magnitude of enthalpy of mixing. The effect of ionic radii is discussed in more detail in the **Section 6.4** and **7** in this chapter.

Table 5. 2: Binary systems AlkF-ThF₄ of (where Alk = Li, Na, K, Rb) are reported in the literature that exhibit minimum enthalpies of mixing at composition X(ThF₄) $\approx$ 0.4.

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System ThF ₄	Method	ΔH^M (kJ mol ⁻¹)	ΔH^M relative increase
LiF	exp.	-10.1	1.970
NaF	calc.	-19.9	1.593
KF	exp.	-31.7	
RbF	n/a	n/a	n/a

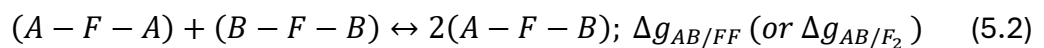
Table 5. 3: Binary systems AlkF-ZrF₄ of (where Alk = Li, Na, K, Rb) are reported in the literature that exhibit minimum enthalpies of mixing at composition X(UF₄) $\approx$ 0.4.

System ZrF ₄	ΔH^M (kJ mol ⁻¹)	Method	ΔH^M rel. inc.
LiF	-18.5	exp.	2.171
NaF	-40.2	exp.	1.354
KF	-54.4	exp.	1.149
RbF	-62.6	exp.	

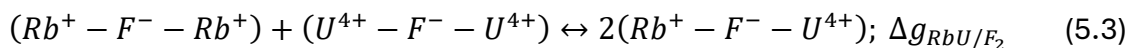
5.4 Thermodynamic modelling for liquid solution

The quadruplet approximation in the quasi-chemical model (QCM), proposed by Pelton and Chartrand (2001) [60] was used to model the excess Gibbs energy of the liquid phase. The later model introduced the quadruplet approximation [28], which consists of two sub-lattices, one consisting of cations A and B (representing U⁴⁺ and Rb⁺) and anion F⁻ (in this work only fluoride anion is present). The quadruplet is the fundamental unit in this updated model. In previous models, i.e. QCM pair approximation, either the first-nearest neighbour (FNN) interactions or the second-nearest neighbour (SNN) were modelled to be the dominant influence on the excess terms. The quadruplet approximation is updated and treats FNN and SNN interactions simultaneously for determining optimised excess parameters of the liquid solution.

The transfer reaction between FNN and SNN pairs is expressed as:



or



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$\Delta g_{RbU/F}$ is an empirical parameter and may be composition dependant, if $\Delta g_{RbU/F_2} = 0$ then random mixing occurs, if $\Delta g_{RbU/F_2} < 0$, then Eq. 3 is displaced to the right with (Rb⁺-F⁻-U⁴⁺) pairs becoming predominant.

The Gibbs energy change $\Delta g_{AB/F}$ associated with the SNN-FNN reaction is given by:

$$\Delta g_{RbU/F_2} = \Delta g_{RbU/F_2}^0 + \sum_{i \geq 1} g_{RbU/F_2}^{i0} x_{RbU/F_2}^i + \sum_{j \geq 1} g_{RbU/F_2}^{j0} x_{RbU/F_2}^j \quad (5.4)$$

Where $\Delta g_{RbU/F_2}^0$ and g_{RbU/F_2}^{i0} are composition independent coefficients that may vary with temperature. Note that the terms with subscript _{RbU/F₂} and _{URb/F₂} represent the same pairs and can be used interchangeably. x_{RbU/F_2}^i is composition dependant function, defined as the fraction to cation-cation pair mole fractions X_{RbRb} , X_{RbU} and X_{UU} :

$$x_{RbU/F_2} = \frac{X_{RbRb/F_2}}{X_{RbRb/F_2} + X_{RbU/F_2} + X_{UU/F_2}} \quad (5.5)$$

As the composition of RbF-UF₄ binary systems changes, the quadruplet approximation model must maintain other parameters to satisfy the conservation of charge whilst simultaneously considering how the FNN and SNN coordination number varies. By assuming the cation SNN coordination number and the charges of cation/anion remain constant, the anion SNN coordination number is fixed in the quadruplet by:

$$\frac{q_{Rb}}{Z_{RbU/F_2}^{Rb}} + \frac{q_U}{Z_{RbU/F_2}^U} = \frac{q_F}{Z_{RbU/F_2}^F} + \frac{q_F}{Z_{RbU/F_2}^F} \quad (5.6)$$

Where q_i are the charges of anions and cations, and $Z_{RbU/FF}^i$ are the SNN coordination number of the respective ion in each quadruplet. For each both end members, the quadruplet formations include (U⁴⁺-F⁻-U⁴⁺), (Rb⁺-F⁻-Rb⁺), (Rb⁺-F⁻-U⁴⁺) SNNs. Their excess Gibbs energy expressions are expressed $\Delta g_{RbRb/F_2}$, $\Delta g_{RbU/F_2}$ and $\Delta g_{UU/F_2}$.

The current work introduces a mixture of U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} into the pure liquid UF₄ as the same complexes and surrogate complexes were identified in recent Raman spectroscopy studies with FLiNaK and FNaK [142] and UF₄/ZrF₄. This permits three different compositions of second nearest neighbour-short range ordering (SNN-

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SRO). U_v^{4+} is the five-coordinated U^{4+} , corresponding to the $[UF_5]^-$ “complex-anion”, U_{vi}^{4+} is the six-coordinated U^{4+} , corresponding to the $[UF_6]^{2-}$ “complex-anion” and U_{vii}^{4+} is the seven-coordinated U^{4+} , corresponding to the $[UF_7]^{3-}$ “complex-anion”. Other U complexes have been identified in molten salt mixtures, such as the dimer $[U_2F_{14}]^{6-}$, but has the same ordering composition as $[UF_7]^{3-}$. For the sake of simplicity, $[U_2F_{14}]^{6-}$ has been excluded from the current model, but could be readily included in future work, for example, if future experimental data justify assigning it distinct thermophysical or electrochemical properties from $[UF_7]^{3-}$.

For the model to maintain mass balance and conservation of charge, the three different uranium complexes balance with the according Rb^+ cations as SNNs. Following this methodology, the following complexes $[UF_5]^-$, $[UF_6]^{2-}$ and $[UF_7]^{3-}$ have SRO at compositions at $X(UF_4)$ at 0.5, 0.333 and 0.25 respectively. The results show that this model excluding any dimers can satisfactorily reproduces all experimental phase diagram data and predicted enthalpy of mixing.

As this model incorporates various uranium cations, pure UF_4 liquid becomes a mixture of U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} cation species and respectively F^- anions. From the Raman spectroscopy data mentioned previously with increasing ZrF_4 , it was assumed that the U_v^{4+} is the dominant species. Further justification of the dominant species having maximum SRO at the composition of 50 mol% in the RbF binary salt mixtures, seen by general deep eutectic at $0.44 \geq X(UF_4) \geq 0.55$. Therefore, to have negligible amounts of U_{vi}^{4+} and U_{vii}^{4+} inside this range, the liquid end-members U_vF_4 , $U_{vi}F_4$ and $U_{vii}F_4$ have been destabilised, a positive Gibbs energy contribution has added as shown in **Table 5.8**, to vary the complexes with composition. The small contribution to the entropy of configuration due to the mixing of the different cationic uranium species does not affect the melting points or enthalpy of fusion of UF_4 .

The resulting molten salt binary system has the Gibbs free energy calculation by the Factsage software by summing the Gibbs free energies of the various quadruplets along with the energy contributed by the configurational entropy

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resulting from the distribution of the quadruplets on the lattice sites as expressed below:

$$G = \sum_{i=U_v U_{vi} U_{vii}} \sum_{j=Rb} \sum_{k=F} n_{ij/kk} g_{ij/k}^0 - T \Delta S^{config} \quad (5.7)$$

Where $n_{ij/kk}$ is the number of moles of the ij/kk quadruplet, $g_{ij/k}^0$ is the molar Gibbs free energy of the ij/k quadruplet, and ΔS^{config} is the configurational entropy of mixing. A definitive mathematical description of the entropy term is not presently established; however, an appropriate expression was proposed by Pelton et al. [60]. The approximation was later improved by Chartrand et al. [28] that was able to treat FNN and more recently SNN SRO. $n_{ij/kk}$ is the internal variable which requires a minimisation of the Gibbs free energy of the molten salt binary solution at a known temperature, pressure and composition – this embodies the equilibrium configuration of both the FNN and SNN. Although the SNN numbers are not used to physically characterise the complexes within the salt solution, they are model parameters which allows to define the composition of which maximum SRO occurs for each complex. This is constrained by charge neutrality, by Eq. 5.6 and following Z numbers used in this model in **Table 5.4**.

Table 5. 4: SNN “coordination numbers” for quadruplets ABXX used in the MQMQA for the liquid.

A	B	X	$Z_{AB/XX}^A$	$Z_{AB/XX}^B$	$Z_{AB/XX}^X$	$Z_{AB/XX}^X$
Rb	U _v	F	6	6	2.4	2.4
Rb	U _{vi}	F	3.6	7.2	2.4	2.4
Rb	U _{vii}	F	8.4	2.8	2.4	2.4
U _v	U _{vi}	F	6	7.2	1.36364	1.36364
U _v	U _{vii}	F	6	8.4	1.75	1.75
U _{vi}	U _{vii}	F	7.2	8.4	1.93846	1.93846

The modified solution model builds on the composition dependent Gibbs energy exchange Eq. 5.4 as there are more than two simple cations; Rb⁺ and U⁴⁺, there are the proposed four; Rb⁺, U_v⁴⁺, U_{vi}⁴⁺ and U_{vii}⁴⁺. Composition variables proposed in Eq. 15 are now accordingly proposed as the following:

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$$\chi_{RbU_v/F_2} = \chi_{RbU_{vi}/F_2} = \chi_{RbU_{vii}/F_2} = X_{Rb_2/F_2} \quad (5.8)$$

$$\chi_{U_vRb/F_2} = \chi_{U_{vi}Rb/F_2} = \chi_{U_{vii}Rb/F_2} = X_{(U_v)_2/F_2} + X_{(U_{vi})_2/F_2} + X_{(U_{vii})_2/F_2} + X_{U_vU_{vi}/F_2} + X_{U_vU_{vii}/F_2} + X_{U_{vi}U_{vii}/F_2} \quad (5.9)$$

$$\chi_{U_vU_{vi}/F_2} = \chi_{U_vU_{vii}/F_2} = \frac{(X_{U_vU_{vi}/F_2} + X_{U_vU_{vii}/F_2})}{(X_{(U_v)_2/F_2} + X_{(U_{vi})_2/F_2} + X_{(U_{vii})_2/F_2} + X_{U_vU_{vi}/F_2} + X_{U_vU_{vii}/F_2} + X_{U_{vi}U_{vii}/F_2})} \quad (5.10)$$

$$\chi_{U_{vi}U_v/F_2} = \chi_{U_{vi}U_{vii}/F_2} = \frac{(X_{U_{vi}U_v/F_2} + X_{U_{vi}U_{vii}/F_2})}{(X_{(U_v)_2/F_2} + X_{(U_{vi})_2/F_2} + X_{(U_{vii})_2/F_2} + X_{U_vU_{vi}/F_2} + X_{U_vU_{vii}/F_2} + X_{U_{vi}U_{vii}/F_2})} \quad (5.11)$$

$$\chi_{U_{vii}U_v/F_2} = \chi_{U_{vii}U_{vi}/F_2} = \frac{(X_{U_{vii}U_v/F_2} + X_{U_{vii}U_{vi}/F_2})}{(X_{(U_v)_2/F_2} + X_{(U_{vi})_2/F_2} + X_{(U_{vii})_2/F_2} + X_{U_vU_{vi}/F_2} + X_{U_vU_{vii}/F_2} + X_{U_{vi}U_{vii}/F_2})} \quad (5.12)$$

As equation 18 represents the total Gibbs free energy on the overall system as a given composition and temperature, the expression for the configurational entropy of mixing (ΔS^{config}) necessitates FNN pair fractions to mitigate convergence between quadruplets and other sets of quadruplets. The parameter ζ is introduced which is defined as the number of quadruplets emanating from the FNN pair, in this case, a Rb⁺-F⁻ or U⁴⁺-F⁻ pair. In other molten salt models using the improved MQMQA, authors have varied ζ , normally to account for the reciprocal systems containing significant differences of anionic radii, such as F⁻ and CO₃²⁻, for example, in the work of Lindberg et al. (2006) [154]. In this work, ζ has been kept equal to 2.4, as proposed by Chartrand et al. [55] for Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺//F⁻, Cl⁻ reciprocal system and by more recent work by Ocádiz-Flores et al. (2021) for the Li⁺, U⁴⁺ // F⁻ system.

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Lastly, the $\Delta g_{RbU/F_2}$ values for all quadruplets were manually optimised, rather than using the OptiSage software, to achieve the best fit with both the previously reported and newly measured phase diagram data. This approach helped maintain the expected enthalpy of mixing and reduced potential errors arising from the entropic parameters used in the fitting process. The $\Delta g_{RbU/F_2}$ coefficients are usually expressed as $A + BT$, where A and B are optimised individually to achieve the possible fit to the data. In this work, as the RbF-UF₄ binary system is more complex, exhibiting three different eutectics, rather than a singular eutectic found in other binary halide salt systems, more coefficients are typically introduced, such as:

$$\Delta g_{RbU/F_2} = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E \cdot T^3 \quad (5.13)$$

5.5 Experimental procedure

5.5.1 Reagent preparation and handling

The reagents used are:

Uranium tetra fluoride (UF₄) anhydrous powder was from International Bio-Analytical Industries (as supplied, 5 g batch, purity 99.99%).

Rubidium fluoride (RbF) powder was from Alfa Aesar (as supplied, 2 g batch, purity 99.975%).

For TGA-DSC calibration the standards reagents used are given in Table 4 prior DSC fluoride experiments.

All materials were handled inside the glovebox which circulated dry argon, and the atmosphere was always maintained at > 5 ppm O₂ and > 2 ppm H₂O during the experimental set-up.

The high purity (99.99%) UF₄ came dehydrated and packaged within a sealed container flooded with argon, initial DSC tests indicated no sign of impurities or abnormal thermodynamic behaviour. The RbF was previously tested by DSC measurement and multiple peaks alongside a lower melting point indicated that the

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RbF was partially hydrated. A Schlenk line and flask were used to isolate the RbF under nitrogen or a strong vacuum. Once a strong vacuum of 2.8 Torr was reached, and the Schlenk flask (with RbF sample inside) was then heated to 513 K via sand bath, it was left for 72 hrs, occasionally flushing the flask with dry nitrogen gas to encourage movement of any static H₂O vapour in the headspace of the flask. This method was deemed successful, and the multiple peaks originally observed in the untreated RbF were eliminated and the melting point and enthalpy of fusion were within literature values of less than 2%. Isolating the dried RbF within the Schlenk flask meant it never was reintroduced to air and could be transferred easily to the glovebox for permanent storage and stored in the glovebox.

All crucibles and lids were cleaned by immersion in a 1:1 ethanol–acetone solution and treated in an ultrasonic bath for 60 minutes at room temperature. After discarding the solution, they were rinsed with distilled water and subsequently placed in anhydrous methanol for a second 60-minute ultrasonic treatment. Finally, once the bulk methanol was discarded, and crucibles and lids were dried in a 333 K oven for 4 hours to ensure complete removal of residual methanol.

5.5.2 Novel crucible

The crucible which contains the sample needs to be first tested. It is one of the most sensitive components within the TGA-DSC unit. A good crucible requires good heat conductivity and inertness with the analysed sample and the DSC holder. The crucibles were specifically produced and designed for fluoride salts investigation, respecting the limits in size of the TGA-DSC unit, having a flat base for good thermal contact to the DSC holder and for its temperature range (298-1273 K).

The sensitivity is related to the enthalpy difference and is optimised when DSC measurement, sensitivity is enhanced when the crucible mass is small compared to the sample mass to limit thermal inertia – good heat conductivity play an important role too. In this case, total crucible mass is 330 mg, whereas commercial crucibles are on the order of 1-10 g, most unsuitable for molten salt fluoride at elevated temperatures. Other institutions have reportedly designed their own

custom crucibles to explore molten salts for this reason, but other parameters such as heat transfer and sensitivity were sacrificed to stay within design specifications as discussed by Piro et al. (2021) [132].

This new design of crucible was used for these experiments, which allows experiments with small salt quantities >20 mg (crucible inner volume: 21.5 mm³) and increases the sensitivity of TGA-DSC results. It was designed specifically at Lancaster University for tests carried out with actinides and lanthanide halides, see **Fig. 5.4 & 5.5**. The challenge here was to meet the specific requirements of fluoride and chloride salts, in terms of sealing, heat conductivity, compatibility, corrosion and temperature range. As the fluoride salts are hygroscopic, air-sensitive, and can be toxic as well for the user and environment, it is important to maintain them in closed environments, to avoid contamination of the salt by oxygen or water vapour from air. A quality sealing is essential to meet these requirements and to avoid composition shift as mass loss occurs through salt vapour. As the main studies of fluoride salts concern at least their melting point and often their liquid behaviour, the crucible needs to achieve its functions at very high temperatures (up to 1273 K). For these constraints Ni-201 was utilised as crucible material and SUS316L for the lid as it was found that utilising the same alloy for both crucible and lid promoted galling when sealing with the hydraulic press and the hermetic seal would be lost. Using matching alloys for both crucible and lid components led to galling during sealing and thus leakage at temperatures above the solidus due to partial volatilisation of the liquid phase.

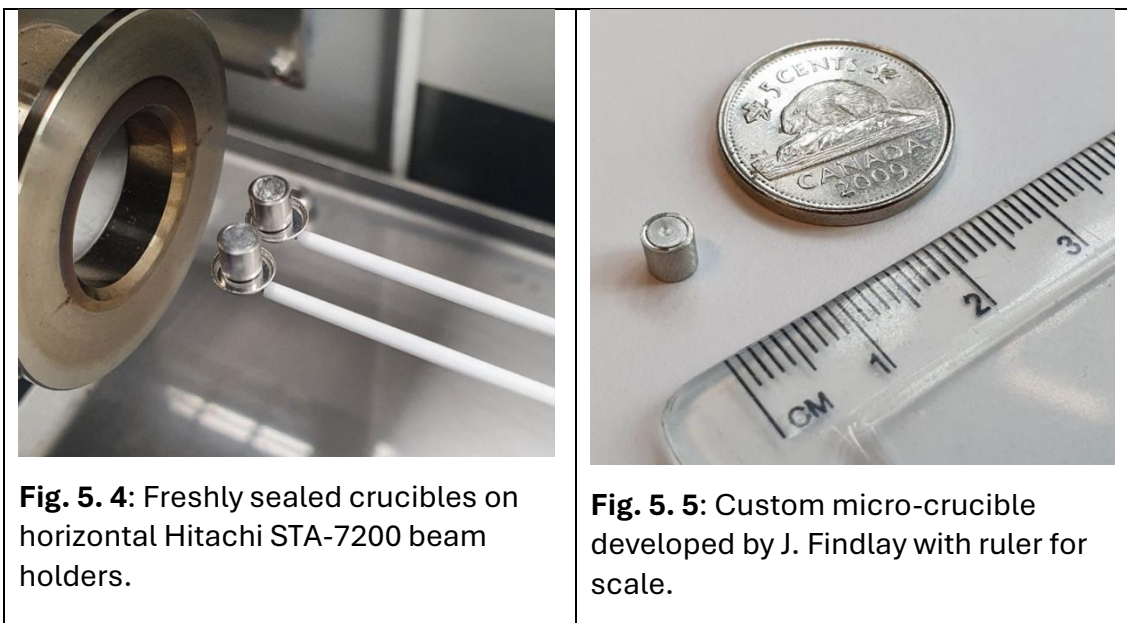


Fig. 5. 4: Freshly sealed crucibles on horizontal Hitachi STA-7200 beam holders.

Fig. 5. 5: Custom micro-crucible developed by J. Findlay with ruler for scale.

5.5.3 DSC Instrumentation and methodology

TGA-DSC measurements were conducted using a Hitachi STA-7200, which enables simultaneous Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). All data were processed using Hitachi Analysis® software. The unit accommodates two crucibles, one for the sample and one reference, with experiments performed under a continuous argon flow (200 mL·min⁻¹) to prevent oxidation.

Calibrations were conducted based on crucible type, temperature range, and sensitivity, using KNO₃, KClO₄, Ag₂SO₄, CsCl, BaCO₃, and Ag as standards, which are chemically compatible with nickel/steel alloy crucibles used in this work, unlike Au or Zn with Pt, which risk alloying with the crucible itself. A blank run with empty crucibles was used to establish the baseline. Baseline drift was observed with frequent use, but the custom crucibles provided high sensitivity and well-defined peaks (as demonstrated in **Fig. 5.8 & 5.9**). Standard salts, as well as pure indium and silver were used as recommended by the literature. This was to prevent any unwanted reaction from typical alloying that can be observed by using standard DSC calibration metals with certain metal crucibles – more details are found in the supplementary material.

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Samples of known RbF-UF₄ composition were loaded into hermetically sealed crucibles inside a glovebox, then transferred directly to the furnace. The furnace was purged with argon for 30 minutes before running four heating cycles (10, 10, 8, and 5 K min⁻¹;) and three cooling cycles (10, 8, 5 K min⁻¹). The first heating cycle data was discarded due to incomplete melting and insufficient homogenisation of the mixture.

TGA measured mass changes during heating/cooling to identify decomposition or volatilisation, while DSC captured heat flow differences between the sample and reference. In this work, however, TGA measurements were used only to identify if the crucible mechanically failed – resulting in mass loss through volatilisation. Endothermic or exothermic transitions were identified by onset and offset peaks, as defined by Sarge et al. (1990) [155]. TGA temperature precision is ± 0.001 K (Charsley et al., 2019) [131], with calibration error being the primary source of uncertainty, due to manual extrapolation of transition temperatures.

5.6 Results

5.6.1 Thermodynamic of pure and intermediate compounds

The thermodynamic data ($\Delta H^\circ_{298.15K}$, $S^\circ_{298.15K}$ and C_P) for all compounds are given in **Table 5.6**. The molar Gibbs free energies of these compounds are expressed as:

$$G(T) = \Delta H^\circ_{298.15K} - T \cdot S^\circ_{298.15K} + \int_{298.15K}^T C_P dT - T \int_{298.15K}^T \frac{C_P}{T} dT \quad (5.14)$$

Where $\Delta H^\circ_{298.15K}$ is the standard enthalpy of formation, $S^\circ_{298.15K}$ is the standard entropy of formation at 298.15K and C_P represents the isobaric heat capacity. To be consistent with NIST-JANAF, the standard state pressure refers to 1 bar.

Thermodynamic data used in previous modelling by Konings (2005) [121] included inaccessible ITU sources, with reported values for UF₄ showing inconsistencies, such as a lower entropy for the liquid than the solid, contradicting fundamental thermodynamic principles. This study instead adopts standard UF₄ data from

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Gurvich [68]. Similarly, anomalous heat capacity values reported for RbF by Barin (1995) [44] were avoided by using Gurvich's data and applying the Neumann–Kopp rule for intermediate compounds to ensure physically realistic behaviour. The thermodynamic properties of RbF-UF₄ end members and intermediate compounds (**Table 5.5**) were refined using a manual iterative CALPHAD method. Formation enthalpies from OQMD [95] and The Materials Project [94] were at 0 K, still showing good agreement with trends observed in this work, with formation enthalpies per g-atom becoming increasingly negative with higher UF₄ content (**Fig. 5.6**).

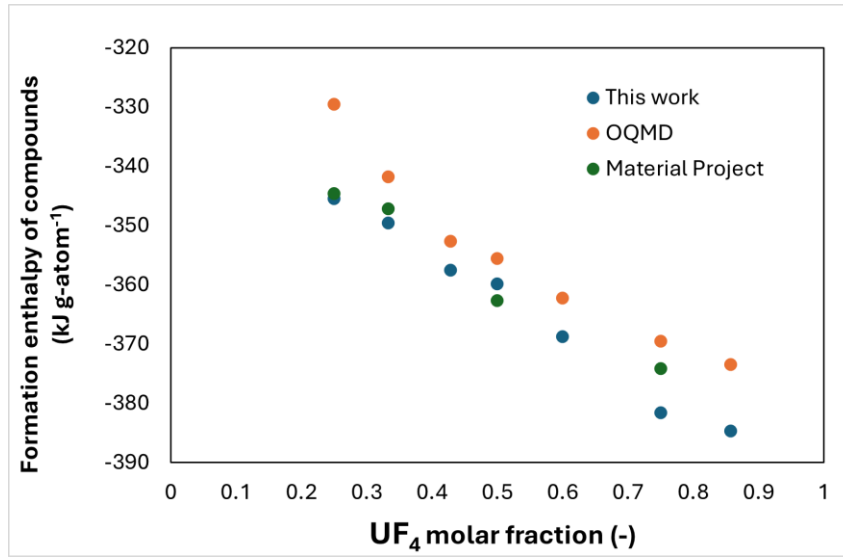


Fig. 5. 6: Formation enthalpy of intermediate compounds (OQMD and MP data calculated at 0 K).

Table 5. 5: Thermodynamic data of the end member RbF-UF₄ and their intermediate compounds.

Compound	<i>T</i> range (K)	$\Delta H_{298.15K}^{\circ}$ (J·mol ⁻¹)	$S_{298.15K}^{\circ}$ (J·mol ⁻¹ ·K ⁻¹)	C_p (J·mol ⁻¹ ·K ⁻¹)	Ref
UF ₄ (s)	298.15-1300	-1920500.0	151.67	$138.865 - 0.03206916 \cdot T - 1401973 \cdot T^{-2} + 2.798899E-5 \cdot T^2$	[68]
	1300-1850			$-731.1297234 - 0.793152089 \cdot T - 278764993 \cdot T^{-2} - 0.000190115 \cdot T^2$	
	1850-2500			167	
UF ₄ (l)	298.15-1190	-1874563.0	186.74	$138.865 - 0.03206916 \cdot T - 1401973 \cdot T^{-2} + 2.798899E-5 \cdot T^2$	[68]

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	1190-1309			$8854.180743 - 10.43385016 \cdot T - 1816697104 \cdot T^{-2} + 0.003519988 \cdot T^2$	
	1309-2500			167	
RbF(s)	298.15-1000	-559700.0	77.70	$42.34987 + 0.02600942 \cdot T + 46610.33 \cdot T^{-2} + 7.981852E-9 \cdot T^2$	[68]
	1000-1220			$221.1816091 - 0.145753209 \cdot T - 46564553.48 \cdot T^{-2} + 3.95922E-5 \cdot T^2$	
	1220-2000			71	
RbF(l)	298.15-1068	-533885.0	101.87	$42.34987 + 0.02600942 \cdot T + 46610.33 \cdot T^{-2} + 7.981852E-9 \cdot T^2$	[68]
	1068-3400			71	
Rb ₃ UF ₇ (s)	298.15-1000	-3775894.831	388.77	$265.91461 + 0.0459591 \cdot T - 1262142.01 \cdot T^{-2} + 2.8012935556E-5 \cdot T^2$	This work.
	1000-1220			$802.4098273 - 0.469328787 \cdot T - 141095633.44 \cdot T^{-2} + 0.00014676559 \cdot T^2$	
	1220-1300			$351.865 - 0.03206916 \cdot T - 1401973 \cdot T^{-2} + 2.798899E-5 \cdot T^2$	
	1300-1850			$-518.1297234 + 0.793152089 \cdot T + 278764993 \cdot T^{-2} - 0.000190115 \cdot T^2$	
	1850-2500			380	
Rb ₂ UF ₆ (s)	298.15-1000	-3152399.559	326.57	$223.56474 + 0.01994968 \cdot T - 1308752.34 \cdot T^{-2} + 2.8004953704E-5 \cdot T^2$	This work.
	1000-1220			$581.2282182 - 0.323575578 \cdot T - 94531079.96 \cdot T^{-2} + 0.00010717339 \cdot T^2$	
	1220-1300			$280.865 - 0.03206916 \cdot T - 1401973 \cdot T^{-2} + 2.798899E-5 \cdot T^2$	
	1300-1850			$-589.1297234 + 0.793152089 \cdot T + 278764993 \cdot T^{-2} - 0.000190115 \cdot T^2$	
	1850-2500			309	

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Rb ₇ U ₆ F ₃₁ (s)	298.15-1000	-15720572.33	1687.20	1129.63909 - 0.01034902 · T - 8085565.69 · T ² + 0.000167989812964 · T ²	This work.
	1000-1220			2381.4612637 - 1.212687423 · T - 334363712.36 · T ² 0.00044507934 · T ²	
	1220-1300			1330.19 - 0.19241496 · T - 8411838 · T ² + 0.00016793394 · T ²	
	1300-1850			-3889.7783404 + 4.758912534 · T + 1672589958 · T ² - 0.00114069 · T ²	
	1850-2500			1499	
RbUF ₅ (s)	298.15-1000	-2521485.492	263.81	181.21487 - 0.00605974 · T - 1355362.67 · T ² + 2.7996971852E-5 · T ²	This work.
	1000-1220			360.0466091 - 0.177822369 · T - 47966526.48 · T ² + 6.758119E-5 · T ²	
	1220-1300			209.865 - 0.03206916 · T - 1401973 · T ² + 2.798899E-5 · T ²	
	1300-1850			-660.1297234 + 0.793152089 · T + 278764993 · T ² - 0.000190115 · T ²	
	1850-2500			238	
Rb ₂ U ₃ F ₁₄ (s)	298.15-1000	-7000378.677	650.41	501.29474 - 0.04418864 · T - 4112698.34 · T ² + 8.3982933704E-5 · T ²	This work.
	1000-1220			858.9582182 - 0.387713898 · T - 97335025.96 · T ² + 0.00016315137 · T ²	
	1220-1300			558.595 - 0.09620748 · T - 4205919 · T ² + 8.396697E-5 · T ²	
	1300-1850			-2051.3891702 + 2.379456267 · T + 836294979 · T ² - 0.000570345 · T ²	
	1850-2500			643	

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RbU ₃ F ₁₃ (s)	298.15-1000	-6484078.556	459.71	458.94487 - 0.07019806 · T - 4159308.67 · T ² + 8.3974951852E-5 · T ²	This work.
	1000-1220			637.7766091 - 0.241960689 · T - 50770472.48 · T ² + 0.00012355917 · T ²	
	1220-1300			487.595 - 0.09620748 · T - 4205919 · T ² + 8.396697E-5 · T ²	
	1300-1850			-2122.3891702 + 2.379456267 · T + 836294979 · T ² - 0.000570345 · T ²	
	1850-2500			572	
RbU ₆ F ₂₅ (s)	298.15-1000	-12306940.0	872.72	875.53987 - 0.16640554 · T - 8365227.67 · T ² + 0.000167941921852 · T ²	This work.
	1000-1220			1054.3716091 - 0.338168169 · T - 54976391.48 · T ² + 0.00020752614 · T ²	
	1220-1300			904.19 - 0.19241496 · T - 8411838 · T ² + 0.00016793394 · T ²	
	1300-1850			-4315.7783404 + 4.758912534 · T + 1672589958 · T ² - 0.00114069 · T ²	
	1850-2500			1073	

5.6.2 Transition temperature measurements of the RbF-UF₄ system

The temperature of the phase equilibria data present consistent values from heating tests, specifically, from the onset and offset temperature of the DSC heating cycles (highlighted in **Fig. 5.7**). No data were taken from the cooling cycle tests due to the supercooling effect - that could be potentially overcome by agitation but could not be implemented with the instruments used in this work. However, the cooling cycles provided far more interpretable DSC peaks which was helpful in determining how many points of equilibria exist for a given composition, demonstrated by **Fig. 5.8**.

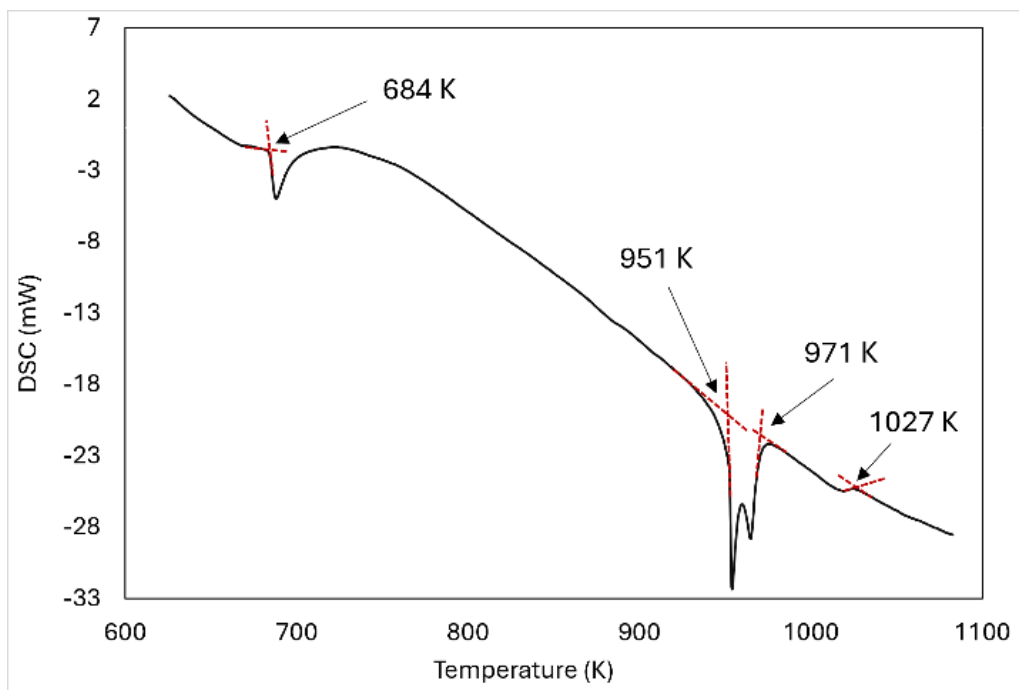


Fig. 5. 7: DSC signal from 2nd heating cycle at 8 K min⁻¹ for composition X (UF₄) = 0.40.

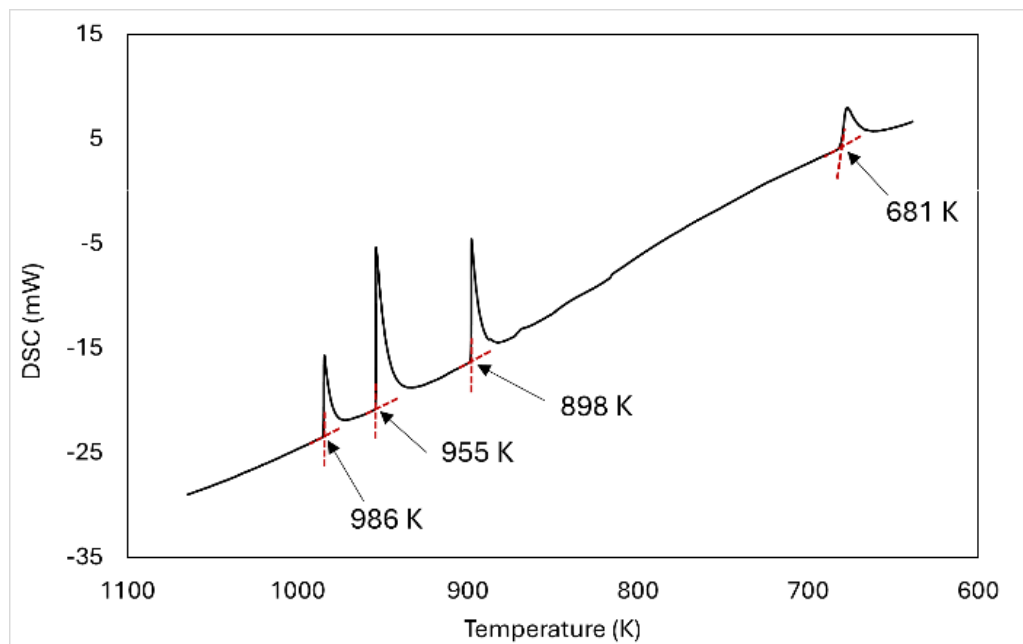


Fig. 5. 8: DSC signal from 1st cooling cycle at 10 K min⁻¹ for composition X (UF₄) = 0.40.

The invariant point data are reported in **Table 5.6** comparing literature data with data gained in this study from DSC signals e.g. **Fig. 5.7 & 5.8**. They concern compositions

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from 0.10 to 0.86 mol per mol and temperatures from room temperatures to 1273 K.

The previous phase diagram data are comparable, suggesting similar behaviour.

Table 5. 6: Comparison of invariant point data. L for liquid phase of the RbF-UF₄ system.

Invariant Phase Reaction	Type of equilibrium	UF ₄ Mole fraction $X(\text{UF}_4)$	Temperature T (K)	Reference
L $\leftrightarrow$ RbF + Rb ₃ UF ₇	Eutectic	0.10	983	[145]
		0.16	987	[144]
		0.10	977 $\pm$ 1	This work
L $\leftrightarrow$ Rb ₃ UF ₇	Congruent melting	0.25	1268 $\pm$ 3	[145]
		0.25	1262	[144]
		0.25	1262 $\pm$ 1	This work
L' + Rb ₃ UF ₇ $\leftrightarrow$ Rb ₂ UF ₆	Peritectic	0.33	1090	[145]
		0.33	1082	[144]
		0.33	1078 $\pm$ 1	This work
L $\leftrightarrow$ Rb ₂ UF ₆ + RbUF ₅	Eutectic	0.435	947 $\pm$ 6	[145]
		0.413	963	[144]
		0.43	948 $\pm$ 1	This work
L' + Rb ₃ UF ₇ $\leftrightarrow$ Rb ₂ UF ₆	Peritectic	0.44	965 $\pm$ 8	[145]
		0.45	982	[144]
		0.46	963 $\pm$ 1	This work
L $\leftrightarrow$ RbUF ₅	Congruent melting	0.5	1007 $\pm$ 5	[145]
		0.5	1002	[144]
		0.5	1007 $\pm$ 1	This work
L $\leftrightarrow$ RbUF ₅ + Rb ₂ U ₃ F ₁₄	Eutectic	0.55	986 $\pm$ 7	[145]
		0.54	973	[144]
		0.55	986 $\pm$ 1	This work
L' + RbU ₃ F ₁₃ $\leftrightarrow$ Rb ₂ U ₃ F ₁₄	Peritectic	0.60	994 $\pm$ 5	[145]
		0.60	993	[144]
		0.60	992 $\pm$ 1	This work
	Peritectic	0.75	1002 $\pm$ 4	[145]

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L' + RbU ₆ F ₂₅ ↔		0.75	1008	[144]
RbU ₃ F ₁₃		0.75	1024 ± 1	This work
L' + UF ₄ ↔	Peritectic	0.86	1104 ± 4	[145]
RbU ₆ F ₂₅		0.86	1083	[144]
		0.86	1127 ± 1	This work

5.6.3 Phase diagram of the RbF-UF₄ system

With data extracted from the DSC curves in this work, thermal analysis data from Thoma et al. (1958) [145] and Friedman et al. (1956) [144], and the quantitatively derived enthalpy of mixing data - the thermodynamics of the liquid solution and solid compounds were both simultaneously calculated through iterations and manual adjustments of the Gibbs energy parameters to fit the liquidus, solidus and eutectic temperatures (given in **Table 5.9**). Extracting the DSC data was relatively straight forward for compositions 0 mol% UF₄ to 80 mol%, but it should be noted that around the congruently melting compound at 25 mol% and above 80 mol% UF₄, the DSC approached its temperature limits. The calculated RbF-UF₄ phase diagram from this work was subsequently compared with data points from the literature (see **Fig. 5.9**).

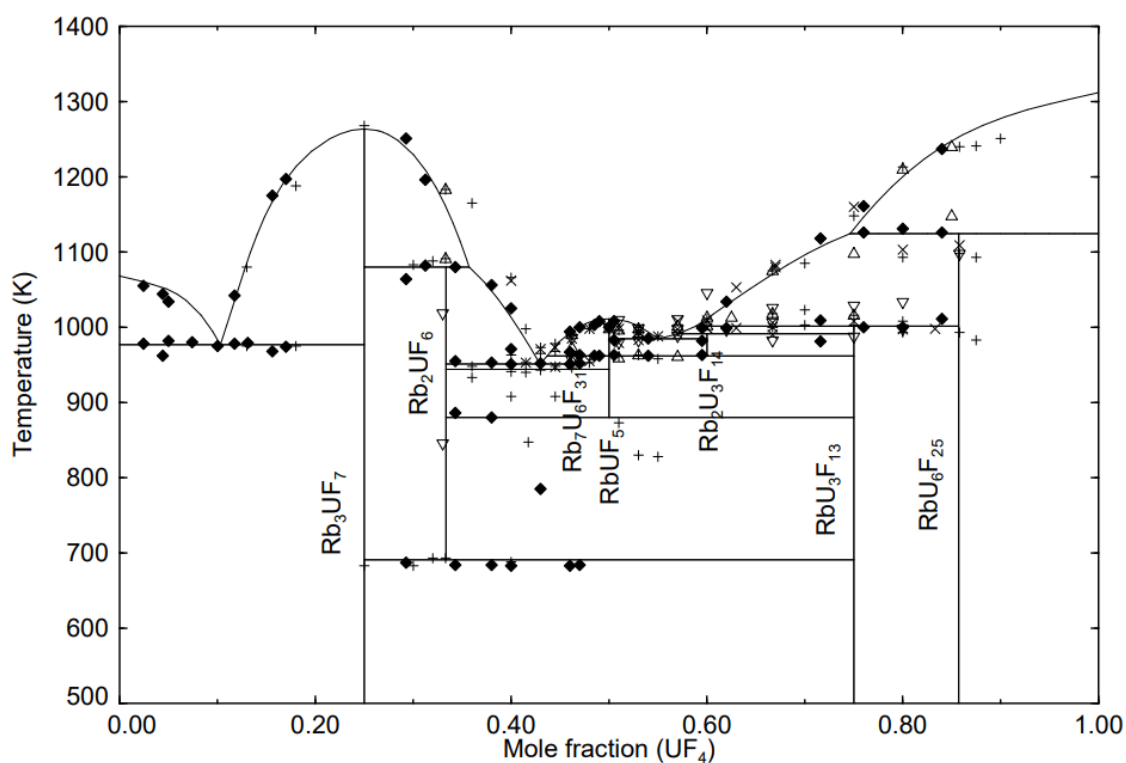


Fig. 5. 9: Calculated RbF-UF₄ phase diagram from this work compared with data points from the literature (◆ this work, + x Thoma et al. (1958) [145], △ ▽ Friedman et al. (1956) [144]).

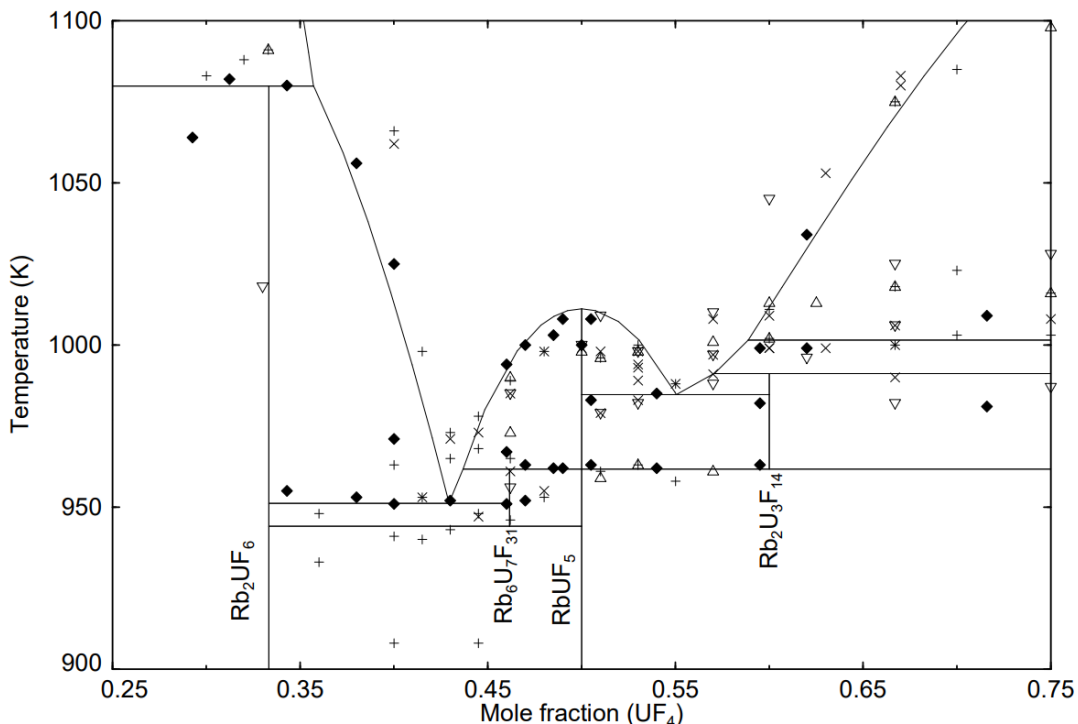


Fig. 5. 10: Zoomed mid-section of calculated RbF-UF₄ phase diagram from this work compared with data points from the literature (◆ this work, + x Thoma et al. (1958)[145], △ ▽ Friedman et al. (1956) [144]).

The compound Rb₃UF₇, which corresponds in composition to a congruent melting phase, was previously reported by Thoma & Grimes (1958). It appears at a liquidus maximum of 1268 K at 25.0 mol% UF₄. Two eutectics were also identified: the first at 948 K and 43 mol% UF₄, and the second at 987 K and 54 mol% UF₄. Strong evidence for the formation of Rb₂UF₆ was observed at 684 K (highlighted in Fig. 13), between 25 and 50 mol% UF₄, consistent with the analogous K₂UF₆ structure recently reported by Schacherl et al. (2021) [104].

Beyond 86 mol% UF₄, experimental data are lacking, so the modelled liquidus in this region was extrapolated to the melting point of pure UF₄. Additional DSC measurements extending above 1273 K, into the single-phase liquid region, would be necessary to confirm the liquidus, solidus, and any solid–solid transitions with higher certainty. The three DSC peaks around 963 K, to the right of the RbUF₅ composition, may reflect partial melting near the third 987 K eutectic, causing the residual non-melted salt to shift toward more UF₄-rich local compositions or they may represent pre-eutectic events.

5.6.4 Enthalpy of mixing

The initial ΔH^M value for LiF-UF₄ was taken from [103], as it remains the only available experimental enthalpy of mixing measurement for the AlkF-UF₄ system to date. The enthalpy of mixing for the remaining AlkF-UF₄ compositions was then estimated using relative increases interpolated between the trends observed experimentally for the AlkF-ThF₄ and AlkF-ZrF₄ systems, seen in **Table 5.2 & 5.3**. This approach aligns more closely with the systematic behaviour observed in other binary molten halide salt systems, for which experimental data exists such as AlkCl-LnCl₃ and AlkF-LnF₃ and similarly for fluoride systems AlkF-LaF₃ and AlkF-YbF₃ systems. The resulting values for the AlkF-UF₄ series yielded more negative enthalpies of mixing, consistent with the limited experimental data, as shown in **Table 5.7** and **Fig. 5.11**.

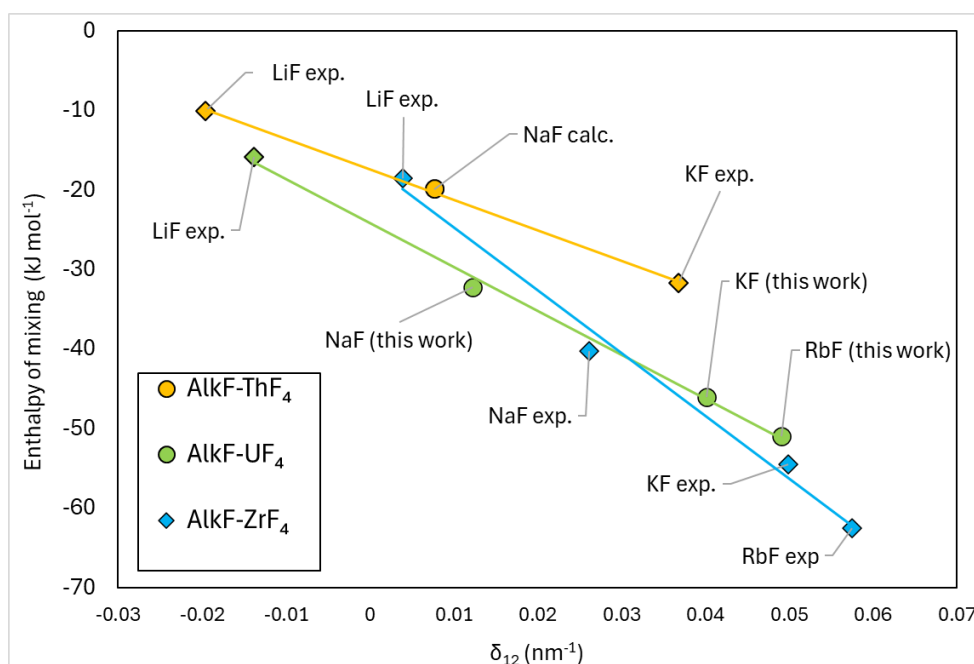


Fig. 5. 11: Experimental, estimated and calculated enthalpy of mixing of Alk-MF₄ systems and re-calculated AlkF-UF₄ systems (excluding LiF-UF₄).

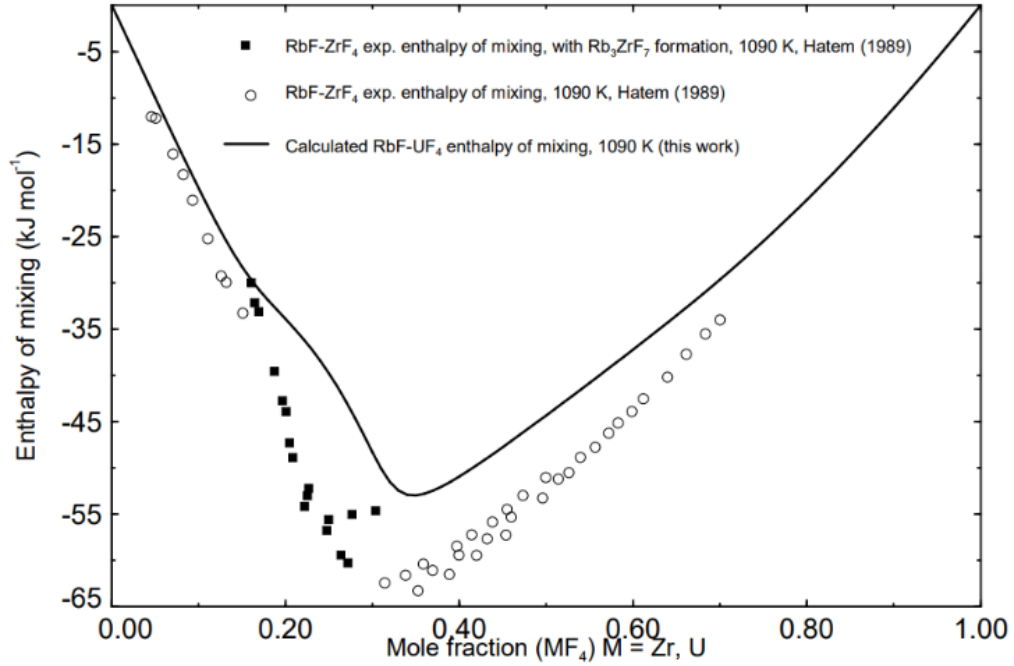


Fig. 5. 12: Experimental enthalpy of mixing data of RbF- ZrF₄ systems with calculated enthalpy of mixing of RbF-UF₄ system.

Table 5. 7: Calculated and re-calculated enthalpy of mixing of the RbF-UF₄ and NaF-UF₄ system using LiF-UF₄ experimental results from [103].

AlkF-UF ₄	Method	ΔH^M (kJ mol ⁻¹)	ΔH^M rel. inc.	Cation IR (nm ⁻¹)	IR rel. inc.
LiF	exp.	-15.9	2.033	0.076	1.342
NaF	calc., this work	-32.3	1.426	0.102	1.353
KF	calc., this work	-46.0	1.109	0.138	1.101
RbF	calc., this work	-52.0		0.152	

5.6.5 Liquid solution and short-range ordering

The liquid solution in this work uses the modified quasi-chemical model in the quadruplet approximation, which incorporates short-range ordering of both first-nearest-neighbours (FNNs) and second-nearest-neighbours (SNNs) by the means of quadruplets as discussed in Section 4. In this work, the Gibbs energy of the three different complexes chosen to represent a pure liquid UF₄ solution were fixed by introducing entropic parameters that kept the composition of the complexes fixed at all temperatures expressed by Eq. 5.18. A small correction was found through

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manual iterations and applied to all standard Gibbs energy functions of the complexes to stabilise and bring them into equilibrium with the pure UF₄. Without this correction, the Gibbs energy functions of the uranium – fluoride complexes would be too negative and therefore dominate and de-stabilise the Rb⁺ ions within the melt.

Table 5. 8: Liquid solution parameters of the RbF-UF₄ system, Gibbs free energies g^0 (J mol⁻¹).

$g_{U_vF_4}^0 = g_{UF_4}^0 + 0.86091 \cdot (T/K)$	(15)
$g_{U_{vi}F_4}^0 = g_{UF_4}^0 + 20.86091 \cdot (T/K)$	(16)
$g_{U_{vii}F_4}^0 = g_{UF_4}^0 + 40.86091 \cdot (T/K)$	(17)
$\Delta g_{RbU_{vii}/F_2} = -48000 - 14.5 \cdot (T/K) \chi_{RbU_{vii}/F_2} + (1.3 \cdot T (T/K) \cdot \ln (T/K) \chi_{U_{vii}Rb/F_2}^3) (18)$	
$\Delta g_{RbU_{vi}/F_2} = -51000 + 15425.9 \chi_{RbU_{vi}/F_2} - 1.1E^{-5} (T^3/K) \chi_{RbU_{vi}/F_2}$	(19)
$\Delta g_{RbU_v/F_2} = -30000 - 0.13 \cdot (T/K) + (-9000 - 1.1(T/K)) \cdot \chi_{U_{vi}Rb/F_2} + 0.7 (T/K) \cdot \ln (T/K) \chi_{U_vRb/F_2}^2 + (0.25 \cdot (T/K) \cdot \ln (T/K) \chi_{U_vRb/F_2}^3)$	(20)

With these parameters, and the thermodynamics of the solid uranium/rubidium containing compounds given in **Table 5.8**, the resulting phase diagram in **Fig. 5.9** was calculated, and the three different eutectics of interest were able to be reproduced with very good agreement from previous literature and the new experimental DSC data presented in this work.

The three standard Gibbs free energy functions of the three uranium complexes in the liquid solutions were set in Eq.'s 5.18-5.20. This gave maximum SRO at different compositions, for [UF₇]³⁻ at X(UF₄) = 0.25, [UF₆]²⁻ at X(UF₄) = 0.33 and [UF₅]⁻ at X(UF₄) = 0.5. The experimental Raman spectroscopy data gathered by Lixin Sun et al. (2019) [142], used mixtures of FLiNaK (LiF: 46.5 mol%, NaF: 11.5 mol%, KF: 42 mol%) with a minute fixed quantity of UF₄ (6 mol%) and increasing quantities of ZrF₄ (2.7 mol% to 27 mol%). Although the work done by Lixin Sun et al.'s [142] main objective was researching the effects of fluorination of UF₄ within the FLiNaK and FKZr melts - as

discussed frequently throughout this work, ZrF₄ is a non-radioactive surrogate for UF₄, given their shared crystallography, oxidation state and similar ionic radii. The inclusion of [UF₇]³⁻, [UF₆]²⁻, and [UF₅]⁻ species in this study is supported by the presence of similarly coordinated zirconium-fluoro complexes observed in FLiNaK and FKZr melts. KF is employed as a proxy for RbF due to their comparable crystallography, similar ionic radii, and closely aligned chemical and thermodynamic properties, as well as the analogous intermediate phases they form with UF₄ and ZrF₄, as widely reported in the literature [156]. The Raman spectroscopy shows as ZrF₄ composition increases to 13.5 mol% to 19.8 mol%, the wavenumber 545 cm⁻¹ assigned to [ZrF₇]³⁻ diminishes and the wavenumbers of 587 cm⁻¹ assigned to [ZrF₆]²⁻ and 595 cm⁻¹ to [ZrF₅]⁻ begins to dominate. In this work, it is hypothesized that [ZrF₆]²⁻ peak and then later the [ZrF₅]⁻ peak will become more pronounced as ZrF₄ mol% further increases past 27.0 mol%, similarly to [UF₆]²⁻ and [UF₅]⁻. The species fraction of uranium complexes in the RbF-UF₄ systems were calculated in this work at 1090 K, See **Fig. 5.13**. On these distributions, one notes the decreases of both [UF₅]⁻ and [UF₆]²⁻ fractions as a function of temperature. Although further experimental testing is required, there is compelling evidence suggesting that this hypothesis is highly likely to be true, and the proposed model in this work represents the most accurate version to date.

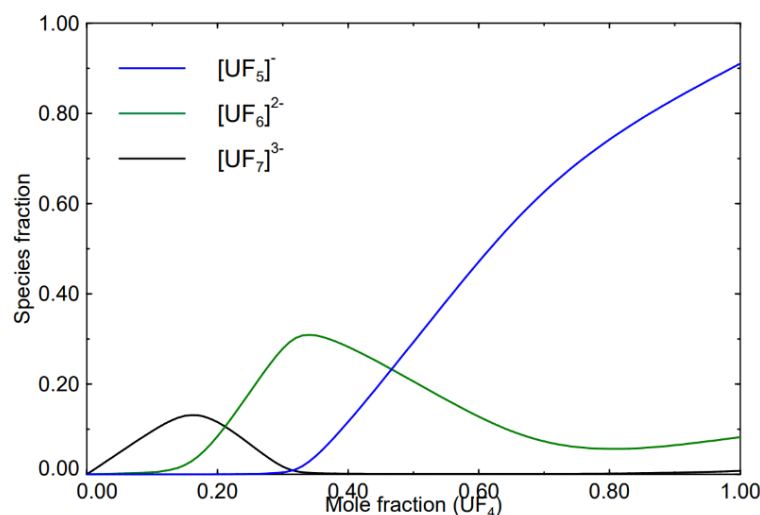


Fig. 5. 13: Species fraction of uranium complexes in the RbF-UF₄ systems calculated in this work, T = 1090 K.

5.6.6 Excess properties

Determining the excess thermodynamic properties of molten salt mixtures is of high interests to this current work. Few experimental investigations of the heat capacity of molten fluoride salt mixtures have been carried out to measure the differentiations of properties. With the few that do exist, excluding UF₄ in the mixture, Roger et al. (1982) [72] reported significant deviations in the heat capacity of molten FLiNaK (46.5 mol% LiF, 11.5 mol% NaF, 42.0 mol% KF) from values predicted by the Neumann–Kopp rule, a trend also observed by Lichtenstein (2020) [73] in more recent measurements of molten FLiBe (66.7 mol% LiF, 33.3 mol% BeF₂). The most recent measurements conducted by Karlsson et al. (2025) [157], with various compositions of the ternary systems NaF – KF – UF₄, heat capacity of the liquid phase was found to be significantly larger than the solid phase, and from ideal NK calculation of the sum of the liquid C_p components – in agreement with the work presented here.

Ocadiz-Flores *et al* (2021) replicated the LiF-UF₄ system with both MD calculations and the CALPHAD approach, revealing the excess properties did not significantly change with composition in the binary system. The ionic radius of U⁴⁺ (6-coordinated – not to be confused with the FNN or SNN coordination numbers) is 0.073 nm⁻¹, and the ionic radius of Li⁺ is 0.076 nm⁻¹. However, with Rb⁺ the ionic radius is 0.152 nm⁻¹ – double that of Li⁺. Increasing the difference between Z/r (charge to radii size) explains the more significant deviations in excess properties. The ionic radii of the anion, in this case, F⁻ is constant at 0.133 nm⁻¹, but increasing the alkali cation radii size, from Li⁺ to Cs⁺, we see an increase in the complexity of the phase diagrams in terms of number of eutectics and solid intermediate compounds, but also higher SRO in the liquid phase combined with a greater thermodynamic stability of solid compounds. Li⁺ also has a closely sized ionic radii to that of U⁴⁺, as first hypothesis by ORNL [80], later reviewed by the joint Argonne National Laboratory (ANL) and

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Kairos report (2021) [81], the more deviations in the Z/r (charge to ratio) size within the molten salt mixtures, the more stable the configuration becomes - this is discussed in more detail in the next section.

The calculated excess molar heat capacity of the liquid solution as a function of UF₄ composition are plotted in **Fig. 5.14** at 1090 K and **Fig. 5.15** at 1300 K, and the excess entropy shown in **Fig. 5.16** at 1090 K and **Fig. 5.17** at 1300 K.

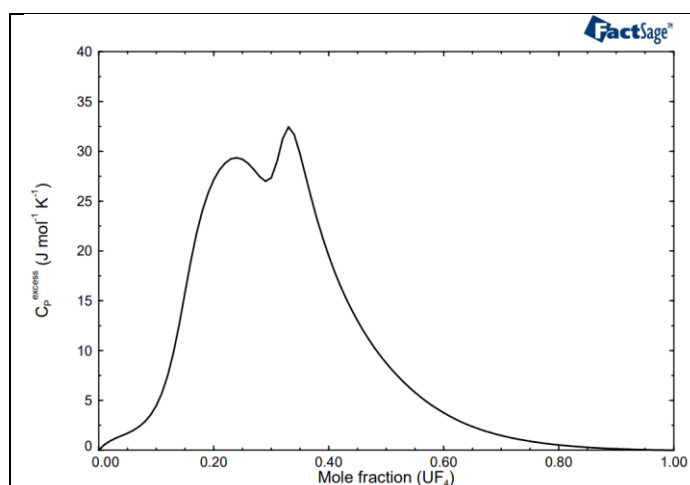


Fig. 5. 14: Calculated excess heat capacity of the liquid solution as a function of UF₄ composition, T = 1090 K.

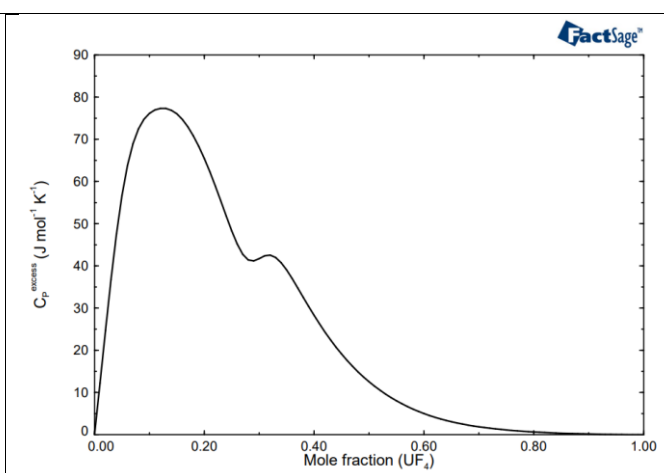


Fig. 5. 15: Calculated excess heat capacity of the liquid solution as a function of UF₄ composition, T = 1300 K.

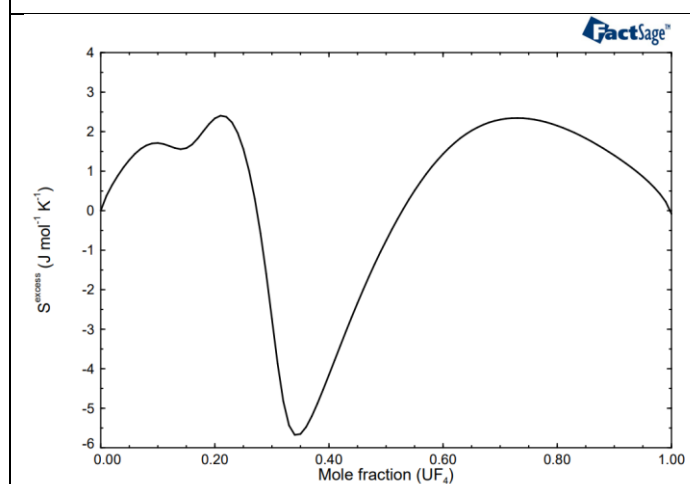


Fig. 5. 16: Calculated excess entropy of the liquid solution as a function of UF₄ composition, T = 1090 K.

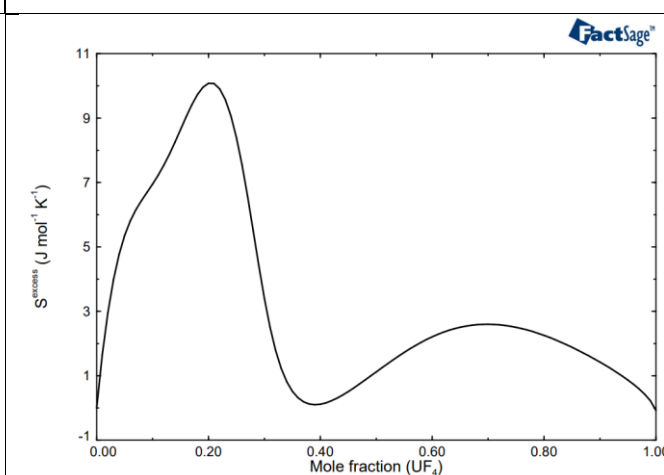


Fig. 5. 17: Calculated excess entropy of the liquid solution as a function of UF₄ composition, T = 1300 K.

The S^{excess} or entropy of mixing shown in **Figs. 5.16 and 5.17** at 1090 K and 1300 K show deviations with a 210 K difference in temperature but share a minimum at composition $X(\text{UF}_4) = 0.35\text{--}0.4$, indicating consistent maximum 2NN SRO between the Rb^+ and U^{4+} cations. At the lower temperature of 1090 K, the calculated S^{excess} is negative between $X(\text{UF}_4) = 0.27\text{--}0.53$ which reveals SRO between Rb^+ and U^{4+} cations that are considerably stronger at this composition at lower temperatures, and at higher temperature, ordering decreases, random mixing of the cations increases – reflected by positive deviations in entropy.

5.6.7 Redox Potential & Corrosion

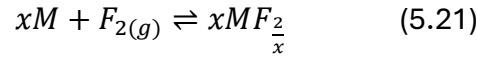
The migration of corrosion products is driven by gradients in Gibbs free energy, predominantly arising from thermally induced chemical potential differentials [75]. In the MSRE, researchers at ORNL had realised the importance of controlling the redox potential of the fuel salt would have significant impact on the corrosion rates of the alloys [78]. For this reason, exotic high-nickel alloys such as Hastelloy-N were developed in parallel at ORNL to mitigate the corrosion issues observed with stainless steels. The alloying metals in stainless steels that enable its anti-corrosion properties, can dissolve and preferentially leach from the surface layers, forming a variety of fluoride species within the molten fuel salt. One of the more well-known alloying components, Cr, which forms a Cr_2O_3 protective layer in stainless steels, was found to be in the some of the higher concentrations within the MSR fuel, and analysis of the alloy confirmed the surface layers were Cr depleted. As well as developing high-nickel alloys, the ORNL researchers improved the redox potential of the fuel salt (65.0 mol% LiF – 29.1 mol% BeF_2 – 5.0 mol% ZrF_4 – 0.4 mol% UF_4) by adding small amounts of UF_3 to make the salt more reducing and was proven to be effective.

However, the potential impact of base salt additions, such as AF (where A = Li, Na, K, Rb), on the redox potential of the system is often overlooked. In this work, we demonstrate that even without altering the $\text{U}^{4+}/\text{U}^{3+}$ ratio, the incorporation of RbF

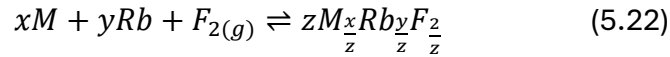
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can yield beneficial effects by lowering the Gibbs free energy of the system, effectively rendering the salt more reducing.

One method to illustrate how the Gibbs free energy change of reactions between the alloying components and various salts versus temperature is through use of an Ellingham diagram. The Gibbs free energy change of these formation reactions per mol of F₂ (g) can be simplified as:



Where x is the stoichiometric coefficient to balance the reaction per mole of pure F₂ gas, M is metal element (M = Mo, Ni, Fe, Cr, Mn, U, Na, Rb). Or in the case of the formation of the molten salt solution in this work:



Where y and z are additional stoichiometric coefficients to balance the reaction per mole of pure F₂ gas for the RbF-UF₄ solution.

The Gibbs free energy of the forward reaction per mole of F₂ (g) in **Eq. 5.21** can then be written as:

$$\Delta G_r^\circ = xG_{MF_{\frac{2}{x}}}^\circ - \left(xG_M^\circ + xG_{F_{2(g)}}^\circ \right) \quad (5.23)$$

Similarly for **Eq. 5.22**, the Gibbs free energy of the forward reaction per mole of F₂ (g) for the RbF-UF₄ solution:

$$\Delta G_r^\circ = zG_{M_{\frac{x}{z}}Rb_{\frac{y}{z}}F_{\frac{2}{z}}}^\circ - \left(xG_M^\circ + yG_A^\circ + xG_{F_{2(g)}}^\circ \right) \quad (5.24)$$

Here, in this work, the newly modelled RbF-UF₄ system, three eutectics at composition X(UF₄) = 0.10, 0.43 and 0.55 where redox potentials are plotted against other pure salts components including alloy corrosion products in **Fig. 5.18**.

UF₃, although may be added in minor quantities to BOG fluoride-based fuel salts, exhibits a more reducing nature than the primary fuel component, UF₄. As illustrated in **Fig. 5.18**, the calculated eutectic compositions substantially lower

the overall redox potential of the melt, creating a more reducing environment than that of pure UF₃.

In **Fig. 5.18**, the composition of the three eutectics, has been used to compare its redox potential against other fluoride salt components. It is noteworthy that UF₃, which is hypothesised to be a small component within all UF₄ containing fuel salts to keep the fuel salt slightly more reducing, is less reducing than the combined liquid solutions with RbF and UF₄. This can provide more insight into controlling salt thermochemistry without the addition of trifluoride actinide salt components.

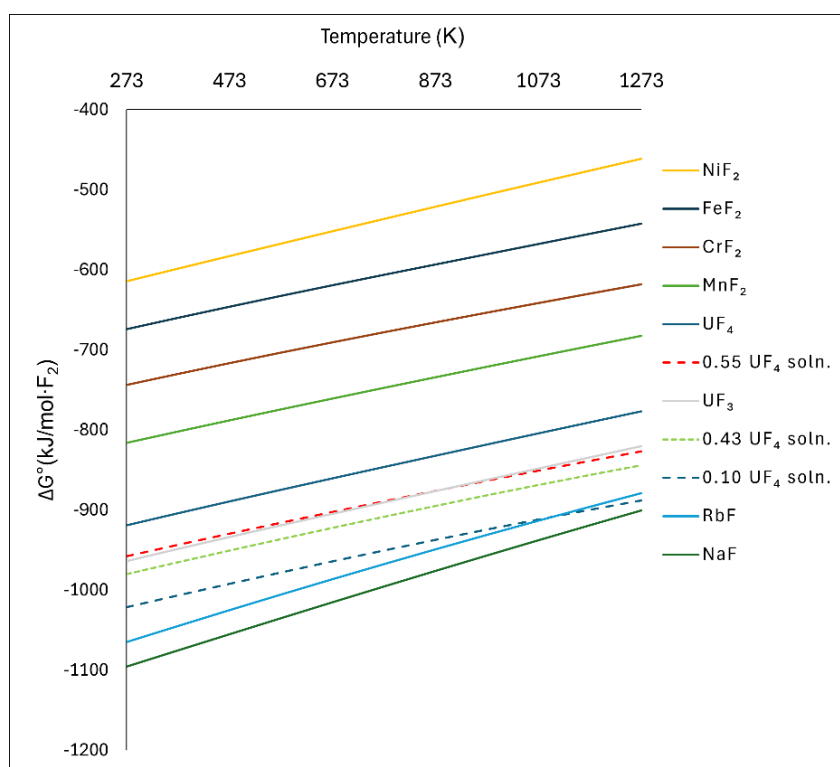


Fig. 5. 18: Standard Gibbs free energy of formation per mole of F₂ for salt components, corrosion products and molten salt solution of the binary molten salt modelled in this work at composition X(UF₄) = 0.10, 0.43 and 0.55.

5.7 Discussion

Previous modelling by Konings et al. [121] used unpublished ITU data that reports unphysical thermodynamic properties for UF₄, including a lower entropy for the liquid than the solid. Due to these inconsistencies, this study adopts the standard UF₄ data from Gurvich [68]. Similarly, anomalous C_p behaviour reported for RbF by

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Barin (1995) [44] is avoided by using Gurvich's data again, ensuring physically consistent heat capacity functions for intermediate compounds via the Neumann–Kopp rule.

Phase equilibria temperatures in this work were determined from the onset and offset of DSC heating cycles (**Fig. 5.7**), as the heating data were more consistent. Cooling data were excluded due to supercooling effects, although the clearer peaks during cooling aided in identifying the number of equilibrium transitions for each composition. The phase equilibria data presented here may have more precision and accuracy over the work by Friedman et al. (1956) [144] and Thoma et al. (1958) [145] as the thermal analysis equipment had its own constraints, using an agitator to limit supercooling effects and encourage crystal growth from cooling – specifically stating in their work it was challenging to read steep liquid lines. To verify the existence and stability of intermediate phases between Rb₂UF₆ and Rb₂U₃F₁₄, samples at relevant stoichiometries should be heated beyond their melting points and then annealed at lower temperatures for extended periods, followed by in situ XRD analysis. More research is needed to verify the stability of the intermediate compounds that exist within the range of the three eutectics in the RbF-UF₄ binary system i.e. $0.10 \leq X(\text{UF}_4) \leq 0.55$ if it is to be considered for a candidate fuel salt or part of ternary or higher order fuel salt system. Concerns may rise from determination of the quantities, types of crystal growth and therefore the properties of the solid phases during fuel fabrication or cooling/shutdown scenario of an MSR.

The enthalpy of mixing for the RbF and UF₄ system is estimated using experimental data from other binary halide salts, with interpolation based on the ionic radius of tetravalent cations, specifically between Th⁴⁺ and Zr⁴⁺. This method also accounts for the relative increase in enthalpy observed with heavier alkali fluorides. Greater confidence is placed in this approach, as it reproduces consistent trends in mixing enthalpies seen across experimentally studied systems involving alkali and lanthanide halides, where cation size plays a dominant role in thermodynamic behaviour. The relative increase in mixing enthalpy appears to correlate more strongly with the increasing ionic radii of the Alk⁺ cations when paired with a common trivalent or tetravalent cation (**Table 5.2, 5.3 & 5.7**). Incorporating the most

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reliable enthalpy of mixing data into the manual iterative optimisation of the phase diagram reduces the degrees of freedom which enables more reliable determination of excess heat capacity, entropy terms and other non-ideal thermodynamic properties. In this case, can significantly influences the total Gibbs free energy of the system, providing deeper insights how composition and carrier salt choice can alter the redox potential of the molten salt solution.

Previous ORNL reports from the Aircraft Reactor Experiment (ARE) program [80] and the more recent Kairos & Argonne National Laboratory literature review [81] discuss the role of cations-anion size in the context of Z/r (charge to radius) ratio. Deviations from ideal solutions often arise from negative heats of mixing, where the mixed salt has a lower energy than the pure components and positive excess entropies due to increased lattice disorder when dissimilar sized cations are mixed.

For instance, it was observed in binary mixtures like NaF-ZrF₄, that additional of UF₄ decreased the activity of ZrF₄, but also destabilised itself relative to AlkF mixtures without ZrF₄. Yet, the addition of UF₄ did not have as large as an effect on reducing the activity of ZrF₄ as it did with decreasing concentration of ZrF₄ in the binary AlkF binary mixtures. This behaviour supports the theory that [80] thermodynamic stability in molten salt solutions can be explained by the effective charge-to-radius (Z/r) ratio of the constituent ions.

A flexible molten lattice system will converge towards the lowest energetically favourable cation configuration, increasing electrostatic attraction and warping the lattice, which often increases disorder. These effects explain why activity coefficients are often less than one, and more negative enthalpies of mixing are observed in heavier AlkF series for any experimentally available data on AlkX-MX₄ and AlkX-LnX₃ binary system ($X = F, Cl, Br, I$; $M = Zr, Th, U$). However, as noted in the Kairos report, the difference in Z/r ratio does not account for all non-ideal thermodynamic behaviour. ORNL interpreted this by the additional fluorine ions supplied by UF₄ contribute to complex formation within the salt solution - i.e., SRO. The thermodynamic modelling in this study incorporates such behaviour through the inclusion of $[UF_7]^{3-}$, $[UF_6]^{2-}$, and $[UF_5]^{-}$ complexes, each of which dominates at specific UF₄ mole fractions within the melt. While complex formation can contribute

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to large deviations from non-ideal thermodynamic properties, particularly in systems with differently charged and sized cations (e.g., NaF–ZrF₄), the mixing enthalpy term is typically the dominant factor in systems where cations have larger different Z/r ratios. In the NaF–ZrF₄ system, it is reported they observed [ZrF₇]³⁻ around X(ZrF₄) = 0.25, but in higher concentration they hypothesised that there would be an increase of bridging fluoride ions and no formation [ZrF₅]⁻ ions. While the original hypothesis provided a valuable starting point, it was later revised considering experimental evidence by Lixin Sun (2019) [142] with KF–ZrF₄ (58-42 mol. %, FKZr) mixtures.

The ORNL report further described fluoride salt mixtures in terms of their fluoroacidity, in their example, it is reported in the NaF–ZrF₄ system, that Na⁺ is the fluoride donor (basic) and the Zr⁴⁺ is the fluoride acceptor (acidic). Here, Rb⁺ is the fluoride donor (basic) and U⁴⁺ is the fluoride acceptor (acidic); in this case specifically: [UF₇]³⁻, [UF₆]²⁻, and [UF₅]⁻. The combination of a stronger acid and a stronger base result in a more pronounced interaction between the two upon mixing. Thermodynamically, this is reflected by larger negative deviations from ideal solution behaviour in the resulting mixture. Rubidium's tendency to “donate” its fluoride ion to nearby uranium ions reflects its basicity and helps stabilize the molten salt mixture. Figure 2.3.2 on page 127 of the report [80] presents the acid–base scale for fluoride salts of interest, showing that RbF exhibits a more basic character than LiF. The plots are intended to predict the relative acidity or basicity of a solute in each solvent, enabling estimation of deviations from ideal behaviour and consequently, their relative solubilities. A key application is selecting solvent compositions that mitigate corrosion by preferentially complexing corrosive species rather than corrosion products. This supports the general findings in this study: while the RbF–UF₄ system may exhibit less favourable higher melting points than the LiF–UF₄ system, it may offer greater corrosion resistance to structural alloys. This is attributed to RbF's stronger tendency to form stable complexes with actinide species, rather than promoting the dissolution of alloying elements from structural MSR internal components into the melt, thus helping to extending the lifespan of an operational MSR. A similar conclusion was also proposed by another recent work

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by Ocádiz Flores et al. (2021) [158], who suggested that reducing the total Gibbs free energy of molten salt system should, in theory, enhance their thermodynamic stability. Other recent studies have been proving the impurities have a significant impact on the corrosiveness of the salts, more experimental work should be done to validate further corrosion resistance can be achieved using incorporating heavier AlkF salts. While this may enhance corrosion resistance, thermal MSR designs employing graphite moderation must carefully manage these conditions, as excessively reducing environments can promote the formation of uranium carbide and trigger other detrimental interactions with the graphite moderator [85]. That said, the reducing component responsible for uranium carbide formation was the addition of UF₃ to UF₄-containing FLiBe mixtures, as demonstrated by Toth et al. (1973) [23]. This observation raises intriguing questions about whether molten salt mixtures can be synthesized without UF₃ doping while still maintaining reducing conditions that prevent uranium carbide formation.

5.8 Conclusion

This work provides a comprehensive thermodynamic re-evaluation of the RbF-UF₄ system, validating decades-old historical phase equilibria data and developing a thermodynamic molten salt model incorporating complex uranium species at different compositions of SRO.

Although further experimental validation is needed, the developed thermodynamic model and refined experimental methods present a robust foundation for future investigations of uranium and plutonium salt systems.

The Z/r charge theory does not explain all non-ideal behaviour of components within specific molten salt systems due to the formation of complexes - which the modelling in this work incorporates and can be built upon in the future models incorporating higher order systems, fission products and vapour species.

The results confirm the existence of three eutectics in the RbF-UF₄ system and illustrate contrasts with the simpler LiF-UF₄ binary, emphasising the trade-offs

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between melting points, actinide solubility relevant to MSR fuel design and improving redox potential by lowering the overall Gibbs energy of compositions of interest. That said, ternary and higher order systems including other heavier AlkF salts and alkaline-earth fluoride salts may contribute to lower melting points whilst retaining the benefits of eutectics at higher actinide loading results in more efficient fuel in terms of burnup and neutron economy.

Ultimately, this study advances the knowledge base required to design optimised fuel salts for next-generation molten salt reactors, paving the way for enhanced reactor performance and fuel cycle flexibility.

5.9 Acknowledgements

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5.10 CRediT

Josh Findlay: Writing – original draft, Investigation, data production, Formal analysis, Figures, Modelling

David Leblanc: Administrative organisation, review & editing, Funding acquisition

Claude Degueldre: Supervision, Writing – review & editing, Conceptualization, Funding acquisition

Patrice Chartrand: Supervision, Modelling review, Conceptualization.

Chapter 6: Thermodynamic investigation of the $\text{CeF}_3\text{-UF}_4$ system and the $\text{RbF-MF}_3\text{-UF}_4$ systems ($\text{M} = \text{Ce, Pu}$)

6.1 Abstract

This chapter introduces higher-order systems, building on the thermodynamic assessments of binary systems presented in the previous chapters. To obtain the complete thermodynamic description of the $\text{RbF-CeF}_3\text{-PuF}_3\text{-UF}_4$ system, the final binary interaction $\text{PuF}_3\text{-UF}_4$ was evaluated using $\text{CeF}_3\text{-UF}_4$ as a surrogate, supported by novel DSC analysis to confirm the eutectic temperature. The two ternary systems $\text{RbF-CeF}_3\text{-UF}_4$ and $\text{RbF-PuF}_3\text{-UF}_4$ have been assessed for the first time. The ternary systems exhibit multiple eutectics, some of which present promising compositions in terms of fissile concentration and operating temperature. Thermodynamic modelling was performed using Factsage, employing the CALPHAD method in combination with the MQMQA (modified quasi-chemical model with quadruplet approximation), which retains the various uranium-coordinated complexes identified in the RbF-UF_4 binary system. By introducing Gibbs energy functions for specific complexes rather than relying solely on broad end-member components, the reliability of the model is improved as the system expands in both components and complexity.

6.2 Introduction

Molten salt reactors (MSRs) are one of the chosen Gen-IV nuclear reactor designs that continues to see vast support, research and development across a span of various private companies and federal-level government globally. Out of the Gen-IV designs, which include a variety of different and exotic fuels and coolants, MSRs are the only reactor concept that relies on the fuel being completely liquid. Rather than liquid metal fuels – which was also explored historically – would not yield the same advantage of having a liquid phase that has ionic properties, allowing larger safety

benefits to be adopted, such as, and the main one being fission-product solubility. Having a nuclear fuel in a liquid phase than a solid fuel which is uniform in phase like UO_2 , although can be more complex to predict its properties and model, therefore requiring rigorous experimental investigation and validation, allows for far more inherent safety features. Unlike solid-fuel reactors, which are constrained by fixed geometry and mechanical control structures, MSRs offer significant design flexibility and configurational freedom, enabling a wide spectrum of reactor architectures. This is highlighted in the IAEA 2023 Status of MSR Technology report [26], where there are 4 main classifications; graphite based, homogeneous, heterogeneous and 'other types' where specific design would struggle to fit under the previous three. Other notable historical works by Taube at the Swiss nuclear institute also highlighted that MSRs could be designed specifically for various main purposes, i.e. for maximum electricity production, for direct heating applications or for long-term sustainability and energy security as breeder type reactors [16].

With the wide range of MSR classifications and applications, fuel selection is a central priority, as it defines the thermo-physical, chemical, and neutronic property limits that ultimately shape the entire reactor design. The choice of fuel salt must satisfy not only these performance requirements but also regulatory standards to ensure safety. Key criteria include: an appropriate melting point, sufficient solubility of actinide components, and the ability to retain fission products either in solution or as thermally stable compounds. Additional desirable traits are high heat capacity and thermal conductivity, low vapor pressure with a high boiling point, adequate density to sustain fission, low viscosity, strong resistance to neutron irradiation and corrosion, and a controllable redox potential.

In the literature, prior focus on fluoride fuel salt were inclusive of the lighter alkali-metal fluoride (AlkF) containing mixtures, such as LiF. While LiF-UF_4 binary system exhibits some desirable traits such as simpler phase diagrams with one eutectic and lower melting temperatures than heavier AlkF containing binary systems, the one eutectic offers less degrees of freedom in design and subsequently for LiF containing higher order systems. The enthalpy of mixing for such systems, plays a main contributing factor into the total Gibbs energy of the mixed system, and

therefore the thermal stability of the final mixed solution. Less explored are the heavier AlkF containing systems such as KF and RbF . In this work, we continue the focus on the RbF containing systems from previous chapters, for the novel thermal assessments, yet whilst also providing a benchmark for future works.

Building on from the binary fluoride systems in previous chapters, unexplored ternary systems $\text{RbF-CeF}_3\text{-UF}_4$ and $\text{RbF-PuF}_3\text{-UF}_4$ will be assessed and completed using Calculation of Phase Diagram (CALPHAD) technique with Factsage software version 8.3. These ternary systems have not yet been reported or assessed in the literature. The investigated system demonstrates considerable compositional flexibility at operating temperatures, which may prove advantageous in meeting requirements for other essential fuel properties. Furthermore, the Gibbs energy-based model developed in this chapter can be applied to construct Ellingham diagrams, enabling the evaluation of the salt's redox potential and illustrating the corresponding corrosion tendencies at any selected molten salt composition providing that other attractive characteristics are met, i.e. melting point, fissile component concentration and neutronics.

6.3 Crystallography

Crystallographic data are fundamental for understanding both the structural and physical properties of compounds. These data reveal atomic arrangements, space groups, and lattice parameters, which are essential for evaluating phase diagrams. Documenting such structures is particularly important, as the future development of higher-order systems containing $\text{RbF-CeF}_3\text{-PuF}_3\text{-UF}_4$ binary components may yield intermediate compounds with comparable crystal structures. In cases where structurally compatible phases emerge, their shared crystallography could facilitate interstitial or substitutional cation exchange within a common sublattice. This mechanism would allow continuous solid solutions to form, rather than distinct and separate solid phases.

Table 6.1 summarizes the data available for both the end members and the intermediate compounds studied. Previously highlighted in Chapter 4 of the RbF-

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PuF₃, intermediate compounds of this system are assumed to have the same crystallography as the intermediate RbF-CeF₃ system. This strongly suggests that, within the two broader RbF-CeF₃-UF₄ and RbF-PuF₃-UF₄ ternary systems under study in this chapter, the likelihood of interstitial or substitutional cation exchange within a common sublattice will be minimal or absent.

Table 6. 1: Summary of the crystallographic data of intermediate solid compounds in the RbF-CeF₃-PuF₃-UF₄ system

Fluoride	Space group	ρ (g cm ⁻³)	Ref.
RbF	$Fm\bar{3}m^*$	3.67	Lax (1997) [123]
	$Pm\bar{3}m$	4.53	
UF ₄	$mS60$	6.71	Kern <i>et al</i> (1994) [152]
	<i>or</i> $C12/c1$		
CeF ₃	$CmCm$	6.16	OQMD [95]
PuF ₃	$CmCm$	9.32	OQMD [95]
(Ce, U)F _x (s.s.)	$CmCm$	n/a	This work
(Pu, U)F _x (s.s.)	$CmCm$	n/a	This work
Rb ₃ UF ₇	$Fm\bar{3}m$	3.46	Bacher & Jacob (1980) [159]
Rb ₂ UF ₆	$Cmcm$	5.20	Kruse (1971) [149]
Rb ₇ U ₆ F ₃₁	P6 ₃	6.02	Toma <i>et al</i> (1958) [145]
RbUF ₅	$P2_1/c$	6.12	Yeon <i>et al</i> (2014) [150]
RbU ₃ F ₁₃	$Pmc2_1$	7.013	Yeon <i>et al</i> (2014) [150]
RbU ₆ F ₂₅	P6 ₃	6.91	Mighell <i>et al</i> (1977) [151]
Rb ₃ CeF ₆	$cF208$	3.46	Springer Mat. [160]
Rb ₂ CeF ₅	$oP32$	4.35	Springer Mat. [125]
RbCeF ₄	$oP24$	5.04	Springer Mat. [126]

6.4 Thermodynamic Modelling

The thermodynamic models presented in this work were developed using *FactSage software (version 8.3)* and manual iterative techniques, within the framework of the

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CALPHAD (CALculation of PHase Diagrams) methodology. Optimisation of the Gibbs energy function parameters for all phases in the systems was carried out using available phase diagram and mixing enthalpy data. Data from previous chapter optimising the RbF-MF₃ (where M = Ce, Pu) binary systems and the RbF-UF₄ binary system were used, but in this chapter, to complete the ternary systems RbF-MF₃-UF₄, the MF₃-UF₄ binary systems are assessed.

6.4.1 Thermodynamics of Pure Compounds

The thermodynamic data ($\Delta H_{298.15K}^0$, $S_{298.15K}^0$ and C_P) for all compounds are optimised in this work and are given in **Table 6.2**. The molar Gibbs free energies of these compounds are expressed as:

$$G(T) = \Delta H_{298.15K}^0 - T \cdot S_{298.15K}^0 + \int_{298.15K}^T C_P dT - T \int_{298.15K}^T \frac{C_P}{T} dT \quad (6.1)$$

Where $\Delta H_{298.15K}^0$ is the standard enthalpy of formation, $S_{298.15K}^0$ is the standard entropy of formation at 298.15K and C_P represents the isobaric heat capacity. To be consistent with NIST-JANAF, the standard state pressure refers to 1 bar.

As explained in the preceding RbF-UF₄ chapter, earlier modelling by Konings (2005) [121] relied on inaccessible ITU sources and included inconsistencies in the reported thermodynamic data, for example, UF₄ values with a lower liquid entropy than the solid, which contradicts fundamental thermodynamic principles. In this study, standard RbF, UF₄, CeF₃ and PuF₃ data from Gurvich [68] are adopted instead. Likewise, anomalous heat capacity values for RbF reported by Barin (1995) [44] were avoided by using Gurvich's dataset and applying the Neumann-Kopp rule to intermediate compounds to ensure physically realistic behaviour. The thermodynamic properties of RbF-CeF₃-PuF₃-UF₄ end-members and intermediate compounds (**Table 6.2**) were then refined using a manual iterative CALPHAD approach.

Novel CeF₃-UF₄ DSC data also suggests the stability of CeUF₇ and CeU₂F₁₁ compounds, therefore, due to the high analogous nature of CeF₃ to PuF₃, the PuUF₇

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and PuU₂F₁₁ compounds were included in this work which previous works in the literature, have not included.

Table 6. 2: Thermodynamic data of the end-member RbF-CeF₃-PuF₃-UF₄ and their intermediate compounds.

Compound	T range (K)	ΔH_f° _{298.15K} (J·mol ⁻¹)	S° _{298.15K} (J·K ⁻¹ ·mol ⁻¹)	$C_{p,m} = a + b \cdot T + c \cdot T^{-2} + d \cdot T^2$				Ref
				a	b	c	d	
RbF (s)	298.15 - 1000	-559700	77.70	42.34987	0.02600942	46610.33	7.981852E-9	Gurcich (1994) [68]
	1000 - 1220			221.1816091	-0.145753209	-46564553.48	3.95922E-5	
	1220 - 2000			71.0				
RbF (l)	298.15 - 580	-534789.47	100.83	42.34987	0.02600942	46610.33	7.981852E-9	Gurcich (1994) [68]
	580 - 948			43.0488533	0.017609851	2.08005E-8	1.25875E-5	
	948 - 3401			71.0				
CeF ₃ (s)	298.15 - 1710	-1688913	115.269	106.3991	-0.01977071	-885090.1	2.864938E-5	Gurcich (1994) [68]
	1710 - 2000			133.888				
CeF ₃ (l)	298.15 - 840	-1635787.64	144.379	106.3991	-0.01977071	-885090.1	2.864938E-5	Gurcich (1994) [68]
	840 - 950			4077.388916	-6.708013086	-416935089.9	0.003200064	
	950 - 2000			133.888				
PuF ₃ (s)	298.15 - 1700	-1552264.0	126.11	92.62	0.0288284	-747200	-1.85103E-6	Gurcich (1994) [68]
	1700 - 2000			146.44				
PuF ₃ (l)	298.15 - 770	-1514157.42	144.398	92.62	0.0288284	-747200	-1.85103E-6	Gurcich (1994) [68]
	770 - 950			2407.685645	-4.186583019	-209092191.7	0.002159831	
	950 - 2000			146.44				
UF ₄ (s)	298.15- 1300	-1920500.0	151.67	138.865	-0.03206916	-1401973	2.798899E-5	Gurcich (1994) [68]
	1300- 1850			-731.1297234	-0.793152089	-278764993	-0.000190115	
	1850- 2500			167				
UF ₄ (l) ^a	298.15- 1190	-1874563.0	186.74	138.865	-0.03206916	-1401973	2.798899E-5	Gurcich (1994) [68]
	1190- 1309			-731.1297234	-0.793152089	-278764993	-0.000190115	
	1309- 2500			167				
Rb ₃ CeF ₆ (s)	298.15 - 1000	-3363426.961	413.369	233.44871	0.05825755	-745259.11	2.8673325556E-5	This work
	1000 - 1220			769.9439273	-0.457030337	-140578750.54	0.00014742598	
	1220 - 1710			319.3991	-0.01977071	-885090.1	2.864938E-5	
	1720 - 2000			346.888				

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Rb_2CeF_5 (s)	298.15 – 1000	- 2873539.817	240.669	191.09884	0.03224813	-791869.44	2.8665343704E-5	This work
	1000 – 1220			548.7623182	- 0.311277128	-94014197.06	0.00010783378	
	1220 – 1710			248.3991	-0.01977071	-885090.1	2.864938E-5	
	1720 – 2000			275.888				
RbCeF_4 (s)	298.15 – 1000	-2296546.91	172.969	148.74897	0.00623871	-838479.77	2.8657361852E-5	This work
	1000 – 1220			327.5807091	- 0.165523919	-47449643.58	6.824158E-5	
	1220 – 1710			177.3991	-0.01977071	-885090.1	2.864938E-5	
	1720 – 2000			204.888				
$\text{RbCe}_2\text{CeF}_7$ (s1)	298.15 – 1000	- 4011466.171	273.238	255.14807	-0.013532	-1723569.87	5.7306741852E-5	This work
	1000 – 1220			433.9798091	- 0.185294629	-48334733.68	9.689096E-5	
	1220 – 1710			283.7982	-0.03954142	-1770180.2	5.729876E-5	
	1720 – 2000			338.776				
$\text{RbCe}_2\text{CeF}_7$ (s2)	298.15 – 1000	- 4000734.671	283.238	255.14807	-0.013532	-1723569.87	5.7306741852E-5	This work
	1000 – 1220			433.9798091	- 0.185294629	-48334733.68	9.689096E-5	
	1220 – 1710			283.7982	-0.03954142	-1770180.2	5.729876E-5	
	1720 – 2000			338.776				
Rb_3PuF_6 (s)	298.15 – 1000	- 3239441.738	419.21	219.66961	0.10685666	-607369.01	-1.827084444E-6	This work
	1000 – 1220			756.1648273	- 0.408431227	-140440860.44	0.00011692557	
	1220 – 1700			305.62	0.0288284	-747200	-1.85103E-6	
	1720 – 2000			359.44				
Rb_2PuF_5 (s)	298.15 – 1000	- 2736382.546	261.51	177.31974	0.08084724	-653979.34	-1.835066296E-6	This work
	1000 – 1220			534.9832182	- 0.262678018	-93876306.96	7.733337E-5	
	1220 – 1700			234.62	0.0288284	-747200	-1.85103E-6	
	1720 – 2000			288.44				
RbPuF_4 (s)	298.15 – 1000	- 2180688.646	168.81	134.96987	0.05483782	-700589.67	-1.843048148E-6	This work
	1000 – 1220			313.8016091	- 0.116924809	-47311753.48	3.774117E-5	
	1220 – 1700			163.62	0.0288284	-747200	-1.85103E-6	
	1720 – 2000			217.44				
RbPu_2F_7 (s1)	298.15 – 1000	- 3745396.545	294.92	227.58987	0.08366622	-1447789.67	-3.694078148E-6	This work
	1000 – 1220			406.4216091	- 0.088096409	-48058953.48	3.589014E-5	
	1220 – 1700			256.24	0.0576568	-1494400	-3.70206E-6	
	1720 – 2000			363.88				
RbPu_2F_7 (s2)	298.15 – 1000	- 3734366.545	304.92	227.58987	0.08366622	-1447789.67	-3.694078148E-6	This work
	1000 – 1220			406.4216091	- 0.088096409	-48058953.48	3.589014E-5	

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	1220 – 1700			256.24	0.0576568	-1494400	-3.70206E-6	
	1720 – 2000			363.88				
$\text{Rb}_3\text{UF}_7(\text{s})$	298.15-1000	-3775894.83 1	388.77	265.91461	0.0459591	-1262142.01	2.8012935556E-5	This work
	1000-1220			802.4098273	-0.46932878 7	-141095633.44	0.00014676559	
	1220-1300			351.865	-0.03206916	-1401973	2.798899E-5	
	1300-1850			-518.1297234	+0.7931520 89	278764993	0.000190115	
	1850-2500			380				
$\text{Rb}_7\text{U}_6\text{F}_{31}(\text{s})$	298.15-1000	-15720572.3 3	1687.20	1129.63909	-0.01034902	-8085565.69	0.000167989812 964	This work
	1000-1220			2381.4612637	-1.21268742 3	-334363712.36	0.00044507934	
	1220-1300			1330.19	-0.19241496	-8411838	0.00016793394	
	1300-1850			-3889.7783404	4.75891253 4	1672589958	-0.00114069	
	1850-2500			1499				
$\text{RbUF}_5(\text{s})$	298.15-1000	-2521485.49 2	263.81	181.21487	-0.00605974	-1355362.67	2.7996971852E-5	This work
	1000-1220			360.0466091	-0.17782236 9	-47966526.48	6.758119E-5	
	1220-1300			209.865	-0.03206916	-1401973	2.798899E-5	
	1300-1850			-660.1297234	0.79315208 9	278764993	-0.000190115	
	1850-2500			238				
$\text{Rb}_2\text{U}_3\text{F}_{14}(\text{s})$	298.15-1000	-7000378.67 7	650.41	501.29474	-0.04418864	-4112698.34	8.3982933704E-5	This work
	1000-1220			858.9582182	-0.38771389 8	-97335025.96	0.00016315137	
	1220-1300			558.595	-0.09620748	-4205919	8.396697E-5	
	1300-1850			-2051.3891702	2.37945626 7	836294979	-0.000570345	
	1850-2500			643				
$\text{RbU}_3\text{F}_{13}(\text{s})$	298.15-1000	-6484078.55 6	459.71	458.94487	-0.07019806	-4159308.67	8.3974951852E-5	This work
	1000-1220			637.7766091	-0.24196068 9	-50770472.48	0.00012355917	
	1220-1300			487.595	-0.09620748	-4205919	8.396697E-5	
	1300-1850			-2122.3891702	2.37945626 7	836294979	-0.000570345	
	1850-2500			572				
$\text{RbU}_6\text{F}_{25}(\text{s})$	298.15-1000	-12306940.0	872.72	875.53987	-0.16640554	-8365227.67	0.000167941921 852	This work
	1000-1220			1054.3716091	-0.33816816 9	-54976391.48	0.00020752614	
	1220-1300			904.19	-0.19241496	-8411838	0.00016793394	
	1300-1850			-4315.7783404	4.75891253 4	1672589958	-0.00114069	
	1850-2500			1073				
$\text{CeUF}_7(\text{s})$	298.15-1300	-3541303.83 8	328.939	245.2641	-0.05183987	-2287063.1	5.663837E-5	This work

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	1300-1710			-624.7306234	0.773381379	277879902.9	-0.00016146562	
	1710-1850			-597.2417234	0.793152089	278764993	-0.000190115	
	1850-2500			300.888				
CeU ₂ F ₁₁ (s)	298.15-1300	-5476099.02	468.809	384.1291	-0.08390903	-3689036.1	8.462736E-5	This work
	1300-1710			-1355.8603468	1.566533468	556644895.9	-0.00035158062	
	1710-1850			-1328.3714468	1.586304178	557529986	-0.00038023	
	1850-2500			467.888				
PuUF ₇ (s)	298.15-1300	-3415183.108	332.68	231.485	-0.00324076	-2149173	2.613796E-5	This work
	1300-1700			-638.5097234	0.821980489	278017793	-0.00019196603	
	1700-1850			-584.6897234	0.793152089	278764993	-0.000190115	
	1850-2500			313.44				
PuU ₂ F ₁₁ (s)		-5342429.784	479.45	370.35	-0.03530992	-3551146	5.412695E-5	This work
				-1369.6394468	1.615132578	556782786	-0.00038208103	
				-1315.8194468	1.586304178	557529986	-0.00038023	
				480.44				

^aLiquid uranium tetrafluoride is modelled as an U_v^{4+} , U_{vl}^{4+} and U_{vil}^{4+} mixture, with $g_{U_vF_4}^0 = g_{U_{vl}F_4}^0 + 0.86091 \cdot (T/K)$, $g_{U_{vil}F_4}^0 = g_{U_{vl}F_4}^0 + 20.86091 \cdot (T/K)$ and $g_{U_{vil}F_4}^0 = g_{U_{vl}F_4}^0 + 40.86091 \cdot (T/K)$

6.4.2 Solid Solution Modelling

The Compound Energy Formalism (CEF) is a mathematical formalism, which is often used to describe the thermodynamic properties of solutions that are modelled with sublattice within a mixed solution phase. In this work, the thermodynamic properties of solid solution phases of the fluoride salts are described using the CEF.

Tri and tetra valent halide salts of lanthanides and actinides tend to form complex solid solutions. These solid solutions can be considered to consist of sublattices, with one sublattice containing a cation or vacancy, such as U^{4+} , Pu^{3+} or Va^0 and the other sublattice containing an anion or vacancy, such as F^- or Va^0 – with the vacancy being electro-neutral having no charge.

R. E. Thoma et al. (1974) [161] noted that LaF₃ structures contain interstitial sites, essentially vacancies, into which U^{4+} cations can migrate. In contrast to other studies that treat M^{3+} and Ac^{4+} (where $M = Ce^{3+}$, Pu^{3+} , U^{3+} , $Ac = Th^{4+}$, U^{4+}) as undergoing simple substitutional reactions, this work employs the compound energy formalism to explicitly integrate these vacancies, Va^0 on the cation sublattice. The (MU)F phase

is thermodynamically treated as (M³⁺, U⁴⁺, Va⁰)₁(F⁻)₃, (where M = Ce, Pu in this work) and its Gibbs energy function per mole is given by the following equation:

$$G_m^{\text{MF}_3\text{ss}} = y_{\text{M}^{3+}}^C \cdot {}^0G_{\text{M}^{3+};\text{F}^-}^{\text{MF}_3\text{ss}} + y_{\text{U}^{4+}}^C \cdot {}^0G_{\text{U}^{4+};\text{F}^-}^{\text{MF}_3\text{ss}} + y_{\text{Va}}^C \cdot {}^0G_{\text{Va};\text{F}^-}^{\text{MF}_3\text{ss}} + RT[y_{\text{M}^{3+}} \cdot \ln(y_{\text{M}^{3+}}) + y_{\text{U}^{4+}} \cdot \ln(y_{\text{U}^{4+}}) + y_{\text{Va}} \cdot \ln(y_{\text{Va}})] + G^E \quad (6.2)$$

where ${}^0G_{\text{M}^{3+};\text{F}^-}^{\text{MF}_3\text{ss}}$, ${}^0G_{\text{U}^{4+};\text{F}^-}^{\text{MF}_3\text{ss}}$, ${}^0G_{\text{Va};\text{F}^-}^{\text{MF}_3\text{ss}}$ refers to the respective standard Gibbs energies of (M³⁺)₁(F⁻)₃, (U⁴⁺)₁(F⁻)₃, (Va)₁(F⁻)₃ pure component end-members (highlighted in **Fig. 6.1**), $y_{\text{M}^{3+}}^C$ and $y_{\text{U}^{4+}}^C$ are the lattice site-fraction of each cationic components and G^E is the excess molar Gibbs free energies. The latter can be expressed as:

$$G^E = \sum_i L_{\text{U}^{4+},\text{M}^{3+};\text{F}^-}^i (y_{\text{U}^{4+}}^C - y_{\text{M}^{3+}}^C)^i y_{\text{U}^{4+}}^C y_{\text{M}^{3+}}^C \quad (6.3)$$

The composition triangle for the MF₃ solid-solution model is shown in **Fig. 6.1** with three different corners. The hypothetical compound UF₄ with the UF₃-type structural form located at the neutral line is obtained by 0.75 moles of (U⁴⁺)₁(F⁻)₃ and 0.25 moles of (Va)₁(F⁻)₃.

$$0.75 \text{ U}^{4+} + 0.25 \text{ Va} + 3 \text{ F}^- = \text{U}_{0.75}\text{Va}_{0.25}\text{F}_3 = \text{UVa}_{1/3}\text{F}_4 = \text{charge neutral} \quad (6.4)$$

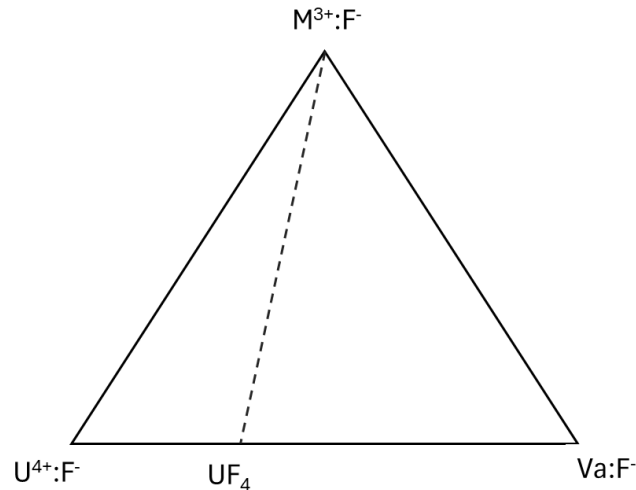


Fig 6. 1: Geometric representation of thermodynamic models for the MF₃ solid-solution phase (M = Ce, Pu).

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The relationship between the Gibbs energies of hypothetical UF₄ and the charged species (U⁴⁺)₁(F⁻)₃ and (Va₁)(F⁻)₃ can be defined as Eq. 4-6:

$${}^0G_{M^{3+};F^-}^{MF_3SS} = {}^0G_{UF_3(s)} \quad (6.5)$$

$${}^0G_{Va:F^-}^{MF_3SS} = a_1 + b_1T \quad (6.6)$$

$${}^0G_{U^{4+};F^-}^{MF_3SS} = {}^0G_{UF_4(s)} + \frac{1}{3} {}^0G_{Va:F^-}^{UF_3SS} + a_2 + b_2T \quad (6.7)$$

Where ${}^0G_{UF_3(s)}$ is the Gibbs energy function of pure UF₃ (s), ${}^0G_{UF_4(s)}$ is the Gibbs energy function of pure UF₄ (s), and parameter a_m and b_n are adjustable parameters determined by the experimental solid-solubility found on the phase diagram. Combining Equation 3 and 6, the term ${}^0G_{Va:F^-}^{UF_3SS}$, is already included within ${}^0G_{U^{4+};F^-}^{MF_3SS}$, due to the stoichiometry from $UVa_{1/3}F_4$. As a result, these contributions cancel, and ${}^0G_{Va:F^-}^{UF_3SS}$ is be set to zero.

The following a_2 and b_2 parameter were set for each binary system CeF₃-UF₄:

$${}^0G_{U^{4+};F^-}^{CeF_3SS} = 22000 - 4.5 \cdot (T/K) \quad (6.8)$$

The finalised Bragg-Williams excess Gibbs energy parameters for the binary system CeF₃-UF₄:

$${}^0L_{Ce^{3+},U^{4+};F^-}^{(CeU)F} = -4 \cdot (T/K) \quad (6.9)$$

$${}^1L_{Ce^{3+},U^{4+};F^-}^{(CeU)F} = 4700 - 2 \cdot (T/K) \quad (6.10)$$

The following a_2 and b_2 parameter were set for each binary system PuF₃-UF₄:

$${}^0G_{U^{4+};F^-}^{PuF_3SS} = 17450 - 3.1 \cdot (T/K) \quad (6.11)$$

The finalised Bragg-Williams excess Gibbs energy parameters for the binary system PuF₃-UF₄:

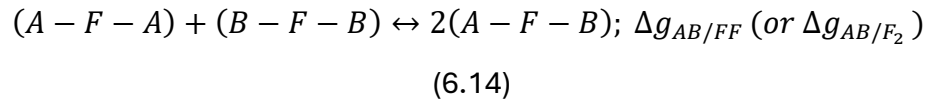
$${}^0L_{Pu^{3+},U^{4+};F^-}^{(PuU)F} = -4 \cdot (T/K) \quad (6.12)$$

$${}^1L_{Pu^{3+},U^{4+};F^-}^{(PuU)F} = 4700 - 2 \cdot (T/K) \quad (6.13)$$

6.4.3 Thermodynamic modelling for liquid solution

The quadruplet approximation in the quasi-chemical model (QCM), proposed by Pelton and Chartrand (2000) [60] was used to model the excess Gibbs energy of the liquid phase. The later model introduced the quadruplet approximation by Chartrand (2001) [28], which consists of two sub-lattices, one consisting of cations A and B and anion F⁻ (in this work only fluoride anion is present). The quadruplet is the fundamental unit in this updated model. In previous models, i.e. QCM pair approximation, either the first-nearest neighbour (FNN) interactions or the second-nearest neighbour (SNN) were modelled to be the dominant influence on the excess terms. The quadruplet approximation is updated and treats FNN and SNN interactions simultaneously for determining optimised excess parameters of the liquid solution.

The transfer reaction between FNN and SNN pairs is expressed as:



$\Delta g_{AB/F_2}$ is an empirical parameter and may be composition dependant, if $\Delta g_{AB/F_2} = 0$ then random mixing occurs, if $\Delta g_{AB/F_2} < 0$, then **Eq. 6.14** is displaced to the right with (A-F-B) pairs becoming predominant.

The Gibbs energy change $\Delta g_{AB/F}$ associated with the SNN-FNN reaction is given by:

$$\Delta g_{AB/F_2} = \Delta g_{AB/F_2}^0 + \sum_{i \geq 1} g_{AB/F_2}^{i0} x_{AB/F_2}^i + \sum_{j \geq 1} g_{AB/F_2}^{j0} x_{AB/F_2}^j \quad (6.15)$$

Where $\Delta g_{AB/F_2}^0$ and g_{AB/F_2}^{i0} are composition independent coefficients that may vary with temperature. Note that the terms with subscript $_{AB/F_2}$ and $_{AB/F_2}$ represent the same pairs and can be used interchangeably. x_{AB/F_2}^i is composition dependant function, defined as the fraction to cation-cation pair mole fractions X_{AA} , X_{AB} and X_{BB} :

$$x_{AB/F_2} = \frac{X_{AB/F_2}}{X_{AA/F_2} + X_{AB/F_2} + X_{BB/F_2}} \quad (6.16)$$

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As the composition of the binary systems changes, the quadruplet approximation model must maintain other parameters to satisfy the conservation of charge whilst simultaneously considering how the FNN and SNN coordination number varies. By assuming the cation SNN coordination number and the charges of cation/anion remain constant, the anion SNN coordination number is fixed in the quadruplet by:

$$\frac{q_A}{Z_{AB/F_2}^A} + \frac{q_B}{Z_{AB/F_2}^U} = \frac{q_F}{Z_{AB/F_2}^F} + \frac{q_F}{Z_{AB/F_2}^F} \quad (6.17)$$

Where q_i are the charges of anions and cations, and $Z_{AB/FF}^i$ are the SNN coordination number of the respective ion in each quadruplet. For each both end members, the quadruplet formations include (A-F-A), (A-F-B), (B-F-B) SNNs. Their excess Gibbs energy expressions are expressed $\Delta g_{AA/F_2}$, $\Delta g_{AB/F_2}$ and $\Delta g_{BB/F_2}$.

The current work re-introduces M_{vi}^{3+} (with coordination number in indices) into the pure liquid MF₃ as the same complex and surrogate complexes were identified in Raman spectroscopy studies with MF₃ and AF mixtures (A = Li, Na, K; M = Ce, Pu) from the previously optimised RbF-CeF₃ and RbF-PuF₃ models by Findlay et al. (2025). This permits one composition of second nearest neighbour-short range ordering (SNN-SRO). There was no evidence for formation of M_{iv}^{3+} four-coordinated M³⁺ within melts, but there was for the six-coordinated complex, corresponding to the [MF₆]³⁻ “complex-anion”.

The current work re-introduces a mixture of U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} into the pure liquid UF₄ as the same complexes and surrogate complexes were identified in recent Raman spectroscopy studies with FLiNaK and FNaK by Sun et al. (2019) [142] and UF₄/ZrF₄ from the RbF-UF₄ model previous assessed by Findlay et al. (2025) [65]. The Raman results from Sun et al. (1019) are shown below with fixed UF₄ concentration and increasing ZrF₄ content working downward in **Fig. 6.2**.

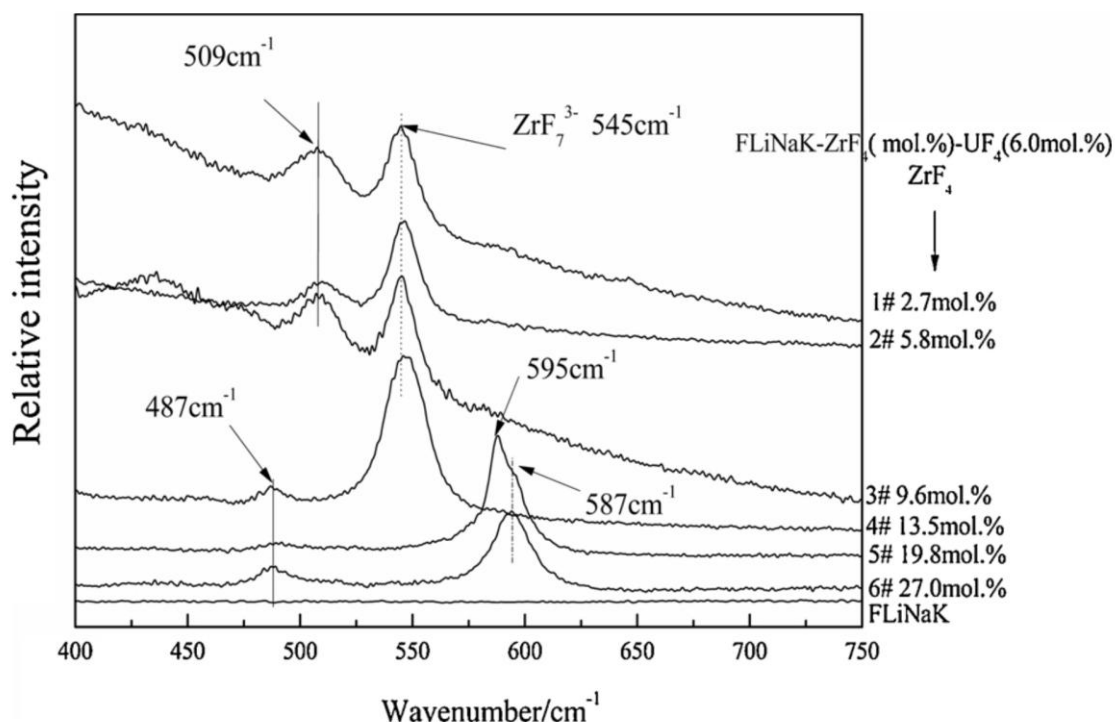


Fig 6. 2: Raman spectra show two bands at 509 cm^{-1} and 545 cm^{-1} for ZrF_4 contents below 9.6 mol%, assigned to UF_x^{4-x} species (e.g. $\text{UF}_7^{3-}/\text{UF}_8^{4-}$) and ZrF_7^{3-} , respectively. With increasing ZrF_4 content and constant UF_4 concentration, the Zr-F band shifts from 545 to 587 cm^{-1} and then to 595 cm^{-1} , corresponding to a transition from ZrF_7^{3-} to ZrF_6^{2-} and finally ZrF_5^- [142].

This permits three different compositions of second nearest neighbour-short range ordering (SNN-SRO). U_v^{4+} is the five-coordinated U^{4+} , corresponding to the $[\text{UF}_5]^-$ “complex-anion”, U_{vi}^{4+} is the six-coordinated U^{4+} , corresponding to the $[\text{UF}_6]^{2-}$ “complex-anion” and U_{vii}^{4+} is the seven-coordinated U^{4+} , corresponding to the $[\text{UF}_7]^{3-}$ “complex-anion”.

For the model to maintain mass balance and for conservation of charge, the three different uranium complexes balance with the according Rb^+ cations as SNNs. Following this methodology, the following complexes $[\text{UF}_5]^-$, $[\text{UF}_6]^{2-}$ and $[\text{UF}_7]^{3-}$ have SRO at compositions at $X(\text{UF}_4)$ at 0.5, 0.333 and 0.25 respectively. The results show that this model excluding any dimers can satisfactorily reproduces all experimental phase diagram data and predicted enthalpy of mixing.

As this model incorporates various uranium cations, pure UF_4 liquid becomes a mixture of U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} cation species and respectively F^- anions. From the Raman spectroscopy data mentioned previously with increasing ZrF_4 , it was

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assumed that the U_v^{4+} is the dominant species. Further justification of the dominant species having maximum SRO at the composition of 50 mol% in the RbF binary salt mixtures, seen by general deep eutectic at $0.44 \geq X(\text{UF}_4) \geq 0.55$. Therefore, to have negligible amounts of U_{vi}^{4+} and U_{vii}^{4+} inside this range, the liquid end-members $U_v\text{F}_4$, $U_{vi}\text{F}_4$ and $U_{vii}\text{F}_4$ have been destabilised, a positive Gibbs energy contribution has added as shown in **Table 9**, to vary the complexes with composition. The small contribution to the entropy of configuration due to the mixing of the different cationic uranium species does not affect the melting points or enthalpy of fusion of UF₄.

The resulting molten salt binary system has the Gibbs free energy calculation by the Factsage software by summing the Gibbs free energies of the various quadruplets along with the energy contributed by the configurational entropy resulting from the distribution of the quadruplets on the lattice sites as expressed below:

$$G = \sum_{i=A} \sum_{j=B} \sum_{k=F} n_{ij/kk} g_{ij/k}^0 - T\Delta S^{\text{config}} \quad (6.18)$$

Where $n_{ij/kk}$ is the number of moles of the ij/kk quadruplet, $g_{ij/k}^0$ is the molar Gibbs free energy of the ij/k quadruplet, and ΔS^{config} is the configurational entropy of mixing. A definitive mathematical description of the entropy term is not presently established; however, an appropriate expression was proposed by Pelton et al. [60]. The approximation was later improved by Chartrand et al. [28] that was able to treat FNN and more recently SNN SRO. $n_{ij/kk}$ is the internal variable which requires a minimisation of the Gibbs free energy of the molten salt binary solution at a known temperature, pressure and composition – this embodies the equilibrium configuration of both the FNN and SNN. Although the SNN numbers are not used to physically characterise the complexes within the salt solution, they are model parameters which allows to define the composition of which maximum SRO occurs for each complex. This is constrained by charge neutrality, by **Eq. 6.10** and following Z numbers used in this model in **Table 6.3**.

Table 6. 3: SNN “coordination numbers” for quadruplets ABXX used in the MQMQA for the liquid.

A	B	X	$Z_{AB/XX}^A$	$Z_{AB/XX}^B$	$Z_{AB/XX}^X$	$Z_{AB/XX}^X$

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Rb	Ce _{vi}	F	2.4	7.2	2.4	2.4
Rb	Pu _{vi}	F	2.4	7.2	2.4	2.4
Rb	U _v	F	6	6	2.4	2.4
Rb	U _{vi}	F	3.6	7.2	2.4	2.4
Rb	U _{vii}	F	8.4	2.8	2.4	2.4
U _v	U _{vi}	F	6	7.2	1.36364	1.36364
U _v	U _{vii}	F	6	8.4	1.75	1.75
U _{vi}	U _{vii}	F	7.2	8.4	1.93846	1.93846
U	Ce _{vi}	F	3	6	1.09091	1.09091
U	Pu _{vi}	F	3	6	1.09091	1.09091

Lastly, the $\Delta g_{AB/F_2}$ of all the quadruplets were manually optimised without the use of Optisage software to fit the previous and new experimental phase diagram data explored in this work – alongside the anticipated enthalpy of mixing. The Gibbs energy function $\Delta g_{AB/F_2}$ within the Factsage software is given by equation: such as:

$$\Delta g_{AB/F_2} = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E \cdot T^3 \quad (6.19)$$

Where coefficients, A-E, are optimised individually to achieve the best possible fit to the data.

In future studies involving different salt mixtures, the same cation may form alternative coordination environments beyond the six-coordinated complex. To ensure thermodynamic consistency, it will be necessary to apply minor corrections, introduced through manual iteration uniformly to the standard Gibbs energy expressions of all fluoride complexes. Careful documentation of these corrections will be essential to accurately assign each coordination species within varying chemical systems for future higher order systems containing this sub-system.

$$\begin{aligned} \Delta g_{\frac{RbCe_{vi}}{F_2}} = & -25000 - (17100 + 0.8 \cdot (T/K)) \cdot \chi_{Ce_{vi}Rb/F_2} - 11200 \cdot \chi_{Ce_{vi}Rb/F_2}^2 + \\ & 1.9 \cdot (T/K) \cdot \ln(T/K) \cdot \chi_{Ce_{iv}Rb/F_2}^3 + 3 \cdot (T/K) \cdot \chi_{RbCe_{vi}/F_2} - 3.2 \cdot (T/K) \cdot \chi_{RbCe_{vi}/F_2}^2 \end{aligned} \quad (6.20)$$

$$\Delta g_{RbPu_{vi}/F_2} = -26000 - 18100 \cdot \chi_{Pu_{vi}Rb/F_2} - 11800 \cdot \chi_{Pu_{vi}Rb/F_2}^2 + 1.9 \cdot (T/K) \cdot \ln(T/K) \cdot \chi_{Pu_{iv}Rb/Cl_2}^3 + 3 \cdot (T/K) \cdot \chi_{RbPu_{vi}/F_2} - 3.2 \cdot (T/K) \cdot \chi_{RbPu_{vi}/F_2}^2 \quad (6.21)$$

$$\Delta g_{RbU_{vii}/F_2} = -48000 - 14.5 \cdot (T/K) \chi_{RbU_{vii}/F_2} + (1.3 \cdot T (T/K) \cdot \ln(T/K) \chi_{U_{vii}Rb/F_2}^3) \quad (6.22)$$

$$\Delta g_{RbU_{vi}/F_2} = -51000 + 15425.9 \chi_{RbU_{vi}/F_2} - 1.1E^{-5} (T^3/K) \chi_{RbU_{vi}/F_2} \quad (6.23)$$

$$\Delta g_{RbU_v/F_2} = -30000 - 0.13 \cdot (T/K) + (-9000 - 1.1(T/K)) \cdot \chi_{U_{vi}Rb/F_2} + 0.7 (T/K) \cdot \ln(T/K) \chi_{U_vRb/F_2}^2 + (0.25 \cdot (T/K) \cdot \ln(T/K) \chi_{U_vRb/F_2}^3) \quad (6.24)$$

$$\Delta g_{Ce_{iv}U/F_2} = -5200 - 0.8 \cdot (T/K) - 4.6 \cdot (T/K) \cdot \chi_{Ce_{vi}U/F_2} - 2.4 \cdot (T/K) \cdot \chi_{UCe_{vi}/F_2} \quad (6.25)$$

$$\Delta g_{Pu_{iv}U/F_2} = -5200 - 0.8 \cdot (T/K) - 4.6 \cdot (T/K) \cdot \chi_{Pu_{vi}U/F_2} - 2.4 \cdot (T/K) \cdot \chi_{UPu_{vi}/F_2} \quad (6.26)$$

6.5 Experimental method

High-purity CeF₃ and UF₄ anhydrous powders were prepared and handled under inert argon in a glovebox. Custom Ni-201 crucibles with SUS316L lids, specifically designed for fluoride salt studies, were used to ensure hermetic sealing, high thermal conductivity, and compatibility at elevated temperatures. All crucibles were rigorously cleaned and dried prior to use. Thermal analyses were performed with a Hitachi STA-7200 TGA-DSC under flowing argon, with calibration against standard

salts and metals to ensure accuracy in enthalpy and temperature determination. Hermetically sealed salt mixtures were loaded in the STA-7200 furnace and subjected to controlled heating–cooling cycles, with TGA used to track volatilisation and DSC to determine melting and solid–solid transitions. This methodology, established in previous chapters by Findlay et al. [33], [35],[34] provides a reproducible and sensitive framework for studying the thermodynamics of $\text{CeF}_3\text{-UF}_4$ mixtures, and serves as the foundation for future extension to other actinide–lanthanide fluoride systems.

6.6 Results & Discussion

6.6.1 The $\text{CeF}_3\text{-UF}_4$ system

There are relatively few DSC or thermal analysis studies on $\text{MF}_3\text{-AcF}_4$ binary systems, where $\text{M} = \text{Ce, U, Pu}$ and $\text{Ac} = \text{Th, U}$. Early phase diagram data for $\text{CeF}_3\text{-ThF}_4$ were reported by Gilpatrick et al. (1970, ORNL) [23] and later refined experimentally and modelled by Beneš et al. (2013). Building on this, Capelli et al. (2015) [162] thermodynamically re-optimised the $\text{PuF}_3\text{-ThF}_4$ and $\text{PuF}_3\text{-UF}_4$ systems, employing CeF_3 as a surrogate for PuF_3 and ThF_4 as a surrogate for UF_4 . More recently, Tosolin et al. (2023) [163] investigated the $\text{PuF}_3\text{-ThF}_4$ system experimentally using DSC and carried out a re-optimisation, while Ard et al. (2023) [164] remodelled the $\text{PuF}_3\text{-UF}_4$ system using a single-sublattice approach for the PuF_3 solid solution. Notably, aside from Beneš' model, which incorporates CeUF_7 and $\text{CeU}_2\text{F}_{11}$, both Capelli and Ard neglect the analogous PuUF_7 and PuThF_{11} compounds, stating they were calculated to be thermodynamically unstable when evaluated using CeUF_7 and CeThF_7 thermodynamic data.

For the first time, the $\text{CeF}_3\text{-UF}_4$ system has been explored with DSC in this work, and remodelled to account for vacancies with the CeF_3 solid lattice structure that smaller U^{4+} cations migrate into and the CeUF_7 and $\text{CeU}_2\text{F}_{11}$ compounds are both stable at elevated temperatures which through DSC signal, provides stronger evidence **Fig 6.3&6.4:**

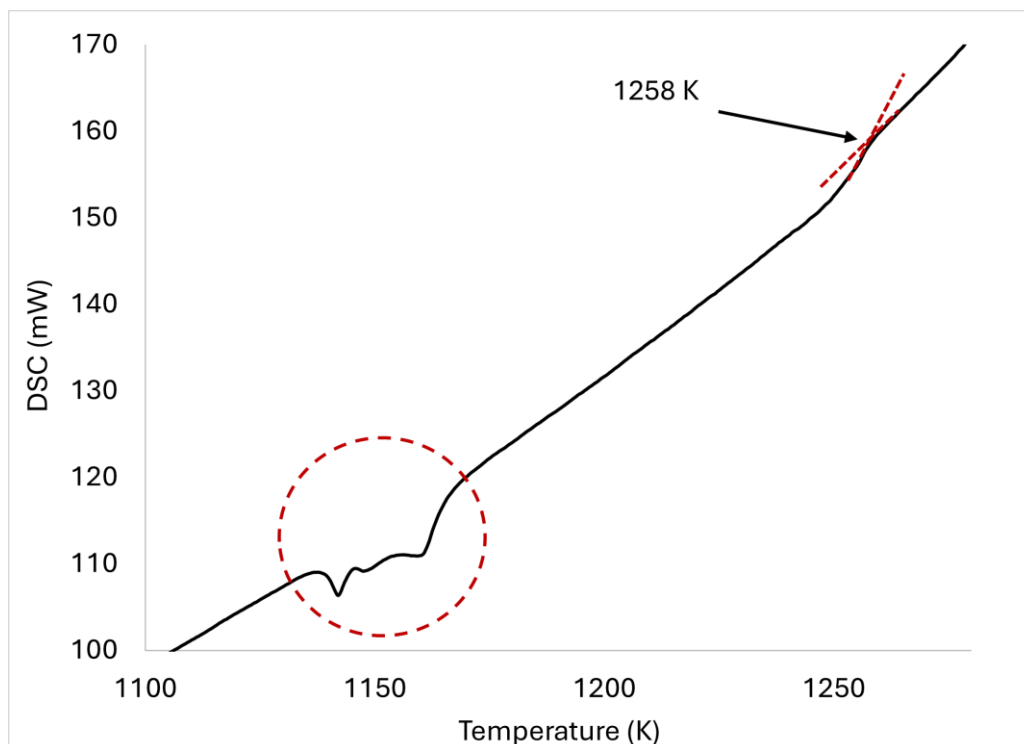


Fig 6. 3: DSC heating cycle at 5 K min^{-1} composition $0.333 \text{ mol UF}_4 - 0.667 \text{ mol CeF}_3$ with high temperature liquidus at 1258 K .

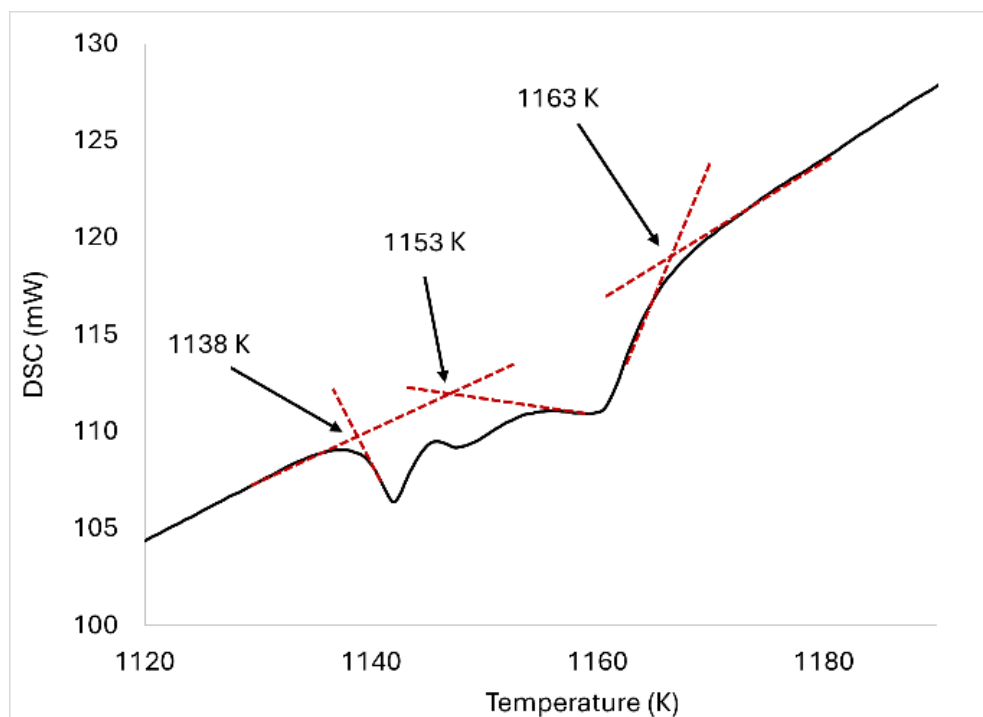


Fig 6. 4: Zoomed DSC heating cycle at 5 K min^{-1} composition $0.333 \text{ mol UF}_4 - 0.667 \text{ mol CeF}_3$ indicating phase transitions from extrapolation of onset and offset temperatures.

In modelling the $\text{CeF}_3\text{-UF}_4$ and $\text{PuF}_3\text{-UF}_4$ binary solid solutions, vacancies were explicitly incorporated on the rare-earth fluoride sublattice rather than assuming a simple substitutional exchange between U^{3+} and U^{4+} cations. This approach more accurately reflects the defect chemistry reported for LaF_3 -type structures by Thoma [161] in the first $\text{UF}_3\text{-UF}_4$ investigation, where interstitial sites and vacancies play a critical role in accommodating charge balance. By integrating vacancies within the compound energy formalism, the models capture both the configurational entropy associated with defect populations and the enthalpic contributions of vacancy–cation interactions. This not only provides a thermodynamically consistent representation of the non-stoichiometry observed experimentally but also improves the predictive capability of the models with respect to physical properties such as ionic diffusion, conductivity, density, and thermal transport. Establishing this framework is essential for extending CALPHAD-based descriptions to more complex actinide fluoride systems, where accurate treatment of defects will underpin future assessments of fuel salt chemistry and performance.

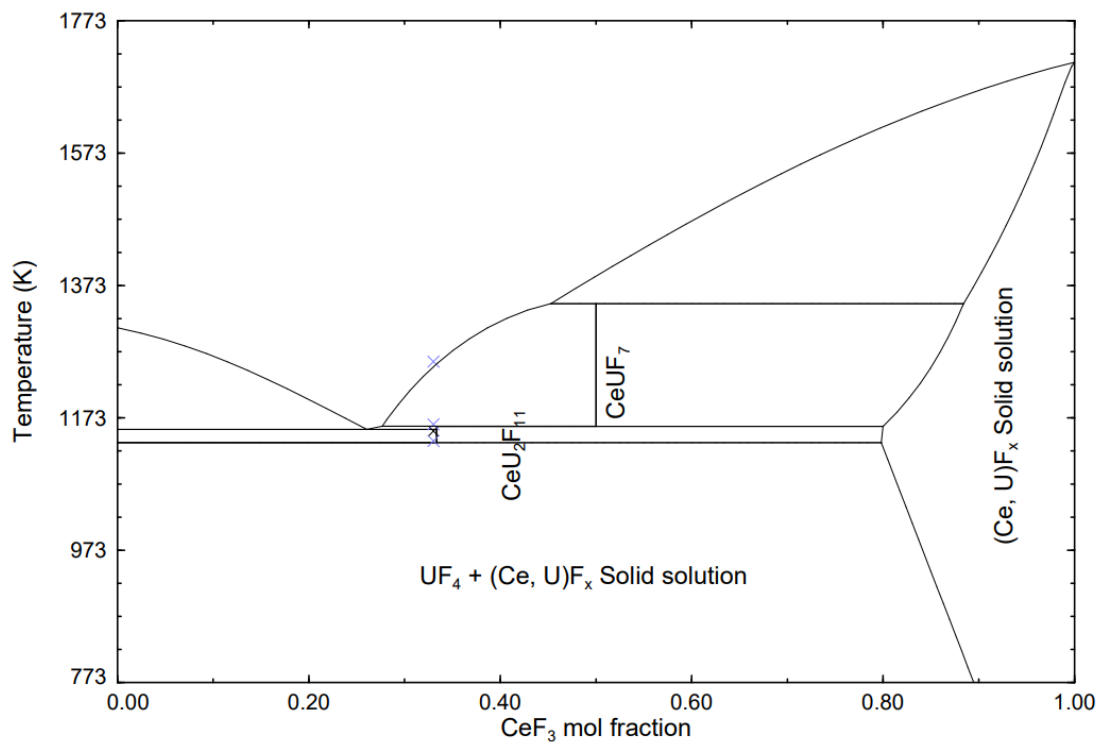


Fig. 6. 5: Optimised $\text{CeF}_3\text{-UF}_4$ phase diagram ~~X~~J. Findlay DSC heating.

6.6.2 The $\text{PuF}_3\text{-UF}_4$ system

Building on from the re-optimisation of the $\text{CeF}_3\text{-UF}_4$ system in the previous section, where the CeUF_7 compound and vacancies within the solid solution were explicitly included, the $\text{PuF}_3\text{-UF}_4$ system has now been remodelled to incorporate the PuUF_7 solid compound and vacancies on the sublattice. This approach departs from earlier models by Capelli [162] and Ard et al. (2023) [164], which relied on simple compositional cation substitution, and follows a methodology more consistent with Tosolin (2021) [163]. The primary objective was to optimise the $\text{PuF}_3\text{-UF}_4$ phase diagram in parallel with the $\text{CeF}_3\text{-UF}_4$ system. As highlighted in the prior chapter (Findlay et al., 2025 [34]), CeF_3 remains one of the most appropriate non-radioactive surrogates for PuF_3 due to its close similarity in cationic radius, enthalpy of fusion, melting point, and crystallography. Consequently, key phase diagram features, including eutectic temperatures and compositions, as well as the stability of intermediate compounds and solid solutions, were expected to align closely between the two systems.

The finalised $\text{PuF}_3\text{-UF}_4$ phase diagram is shown in **Fig. 6.6**.

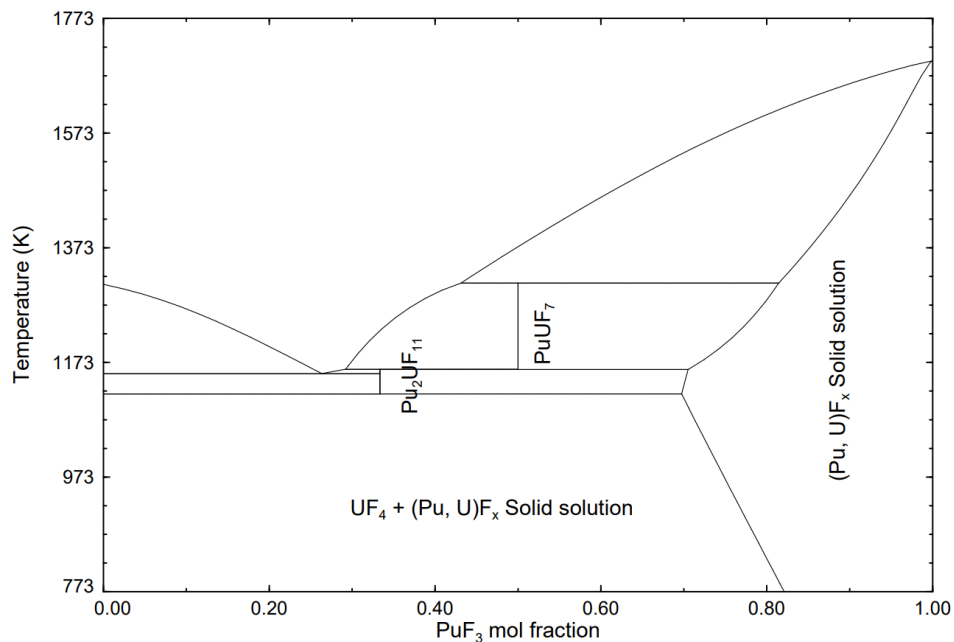


Fig. 6. 6: Optimised $\text{PuF}_3\text{-UF}_4$ phase diagram.

6.6.3 The $\text{RbF-CeF}_3\text{-UF}_4$ system

Optimising the reciprocal sub-binary systems with the $\text{RbF-CeF}_3\text{-UF}_4$ ternary phase diagram using the manual iterative technique combined with determining the various ionic complexes within the molten salts aids in preserving reliability of the model. It is well established that specific molten salts mixtures, do not exhibit a random mixing of cation and anion species, rather they form clusters at specific concentrations, largely in part to each of the species ionic radii/charge ratio. This phenomenon is far more pronounced in MSR fuels where certain alkali metal fluorides are combined with lanthanide and actinide fluoride salts. Known as SRO (short range ordering), the likes Factsage software is built upon, first conceptualised by Pelton, and further developed by Patrice Chartrand in the MQMQA (modified quasi-chemical model in the quadruplet approximation).

The most beneficial aspect of carrying out the Gibbs energy optimisations manually and assigning Gibbs energy functions to each of the complexes within the melts for each binary sub-system, rather than the quicker more common method of assigning the Gibbs energy function to the composition/concentration of a singular end-member component, i.e. $[\text{UF}_5]^-$, $[\text{UF}_6]^{2-}$ and $[\text{UF}_7]^{3-}$ instead of pure UF_4 , is that when the higher order systems, ternary and quaternary, complexity increase but the model maintains reliability. This is also highlighted by previous work in the literature for ternary systems where excess ternary Gibbs energy parameters need to be introduced into the model. These are based on geometric weightings of the mole fractions of each pure end-member component. Such mathematical formula based on the geometric weightings as split into the Kohler, Kohler/Toop, Muggianu and the Muggianu/Toop approximations. The variety are based upon whether the ternary system phase diagram is either asymmetric or symmetric in nature.

In this work, it was found that the composition of the ternary system $\text{RbF-CeF}_3\text{-UF}_4$ measured by DSC, at composition, $\text{RbF-82 mol\%}$; $\text{CeF}_3\text{-4 mol\%}$; $\text{UF}_4\text{-14 mol\%}$, showed a singular thermal event at 907 K, indicating a ternary eutectic, highlighted in Fig. 6:

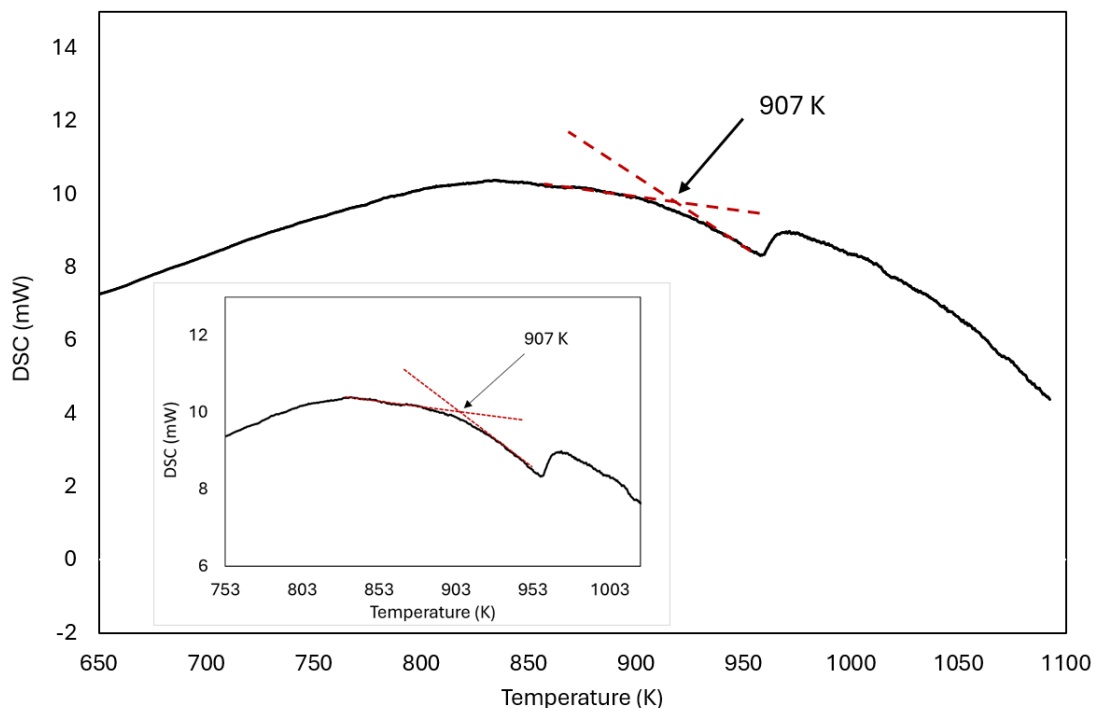


Fig. 6. 7: DSC heating at 10K min^{-1} of mixture, RbF -82 mol%; CeF_3 -4 mol%; UF_4 -14 mol%.

This ternary eutectic was also calculated by the ternary model without the need of any excess ternary Gibbs energy parameters – further highlighting the strength of the manual iterative technique of the Factsage CALPHAD method. The ternary eutectic measured by DSC in this work, is shown below in the quasi-binary system, with constant $\text{CeF}_3 = 4 \text{ mol\%}$ in **Fig 6.7**:

Chapter 6: Thermodynamic investigation of the $\text{CeF}_3\text{-UF}_4$ system and the $\text{RbF-MF}_3\text{-UF}_4$ systems ($\text{M} = \text{Ce, Pu}$)

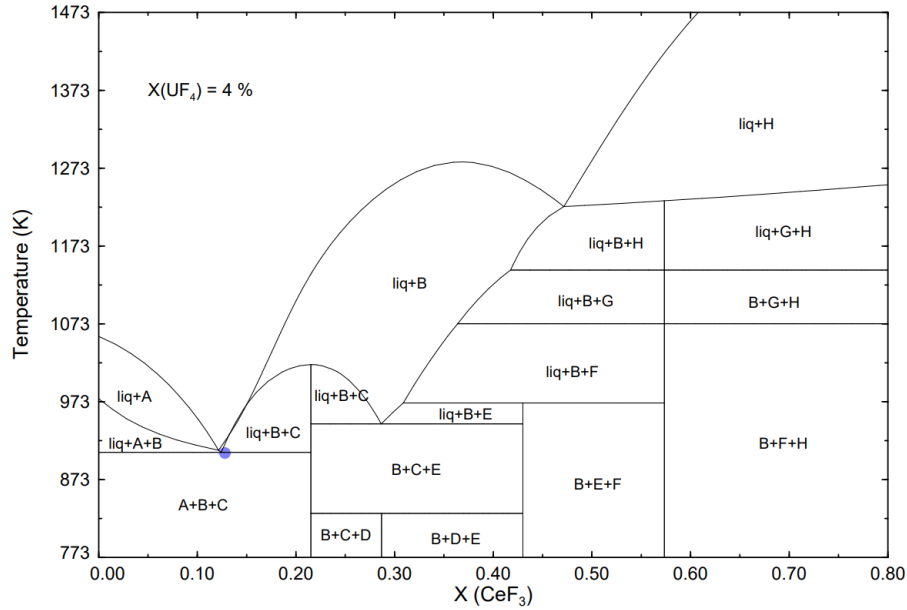


Fig. 6.8: The RbF-CeF_3 pseudo binary phase diagram having fixed composition of $\text{UF}_4 = 4 \text{ mol\%}$. (●) This work – DSC heating. Phase fields: (A) RbF (B) Rb_3UF_7 (C) Rb_3CeF_6 (D) Rb_2CeF_5 (E) RbCeF_4 (F) RbCe_2F_7 (s1) (G) RbCe_2F_7 (s2) (H) $(\text{Rb, Ce}) \text{F}_x$ solid solution

The ternary phase diagram with all four-phase intersection points with the molten salt solutions are given in **Table 6.4** and **Fig. 6.7**:

Table 6. 4: Four-phase equilibria intersection points in the $\text{RbF-CeF}_3\text{-UF}_4$ system

No.	X (UF_4)	X (RbF)	X (CeF_3)	T (K)	Equilibrium	Solid phases in equilibria
1	0.150671	0.51252	0.33681	1255.89	Peritectic	$(\text{Ce, U})\text{F}_x$ (s.s.), Rb_2UF_6 , Rb_3UF_7
2	0.11897	0.489	0.39203	1255.72	Peritectic	$(\text{Ce, U})\text{F}_x$ (s.s.), Rb_2UF_6 , Rb_3UF_7
3	0.00626	0.52052	0.47322	1142.07	Peritectic	RbCe_2F_7 (s2), $(\text{Ce, U})\text{F}_x$ (s.s.), Rb_3UF_7
4	0.73183	0.06233	0.20584	1135.29	Peritectic	UF_4 , $(\text{Ce, U})\text{F}_x$ (s.s.), $\text{CeU}_2\text{F}_{11}$
5	0.72902	0.14978	0.12121	1103.42	Peritectic	UF_4 , $(\text{Ce, U})\text{F}_x$ (s.s.), $\text{RbU}_6\text{F}_{25}$
6	0.35702	0.64283	0.00106	1082.26	Peritectic	$(\text{Ce, U})\text{F}_x$ (s.s.), Rb_2UF_6 , Rb_3UF_7
7	0.0016	0.57793	0.42041	1073.15	Peritectic	RbCe_2F_7 (s1), RbCe_2F_7 (s2), Rb_3UF_7
8	0.42949	0.57041	0.0001	1069.94	Eutectic	$(\text{Ce, U})\text{F}_x$ (s.s.), $\text{Rb}_6\text{U}_7\text{F}_{31}$, Rb_2UF_6
9	0.59019	0.40526	0.00455	1000.69	Peritectic	$(\text{Ce, U})\text{F}_x$ (s.s.), $\text{Rb}_6\text{U}_7\text{F}_{31}$, $\text{RbU}_6\text{F}_{25}$
10	0.56961	0.42749	0.0029	989.4	Peritectic	$(\text{Ce, U})\text{F}_x$ (s.s.), $\text{Rb}_2\text{U}_3\text{F}_{14}$, $\text{RbU}_3\text{F}_{13}$
11	0.55034	0.4477	0.00195	983.47	Eutectic	$(\text{Ce, U})\text{F}_x$ (s.s.), $\text{Rb}_2\text{U}_3\text{F}_{14}$, RbUF_5
12	0.00049	0.64122	0.35829	971.34	Peritectic	RbCe_2F_7 (s1), RbCeF_4 , Rb_3UF_7

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13	0.43671	0.56314	0.00014	961.24	Peritectic	$(\text{Ce, U})\text{F}_x (\text{s.s.}), \text{Rb}_6\text{U}_7\text{F}_{31}, \text{RbUF}_5$
14	0.00056	0.66717	0.33226	944.45	Eutectic	$\text{Rb}_3\text{CeF}_6 (\text{s1}), \text{RbCeF}_4, \text{Rb}_3\text{UF}_7$
15	0.03299	0.84162	0.12538	907.89	Eutectic	$\text{Rb}_3\text{CeF}_6 (\text{s1}), \text{RbF}, \text{Rb}_3\text{UF}_7$

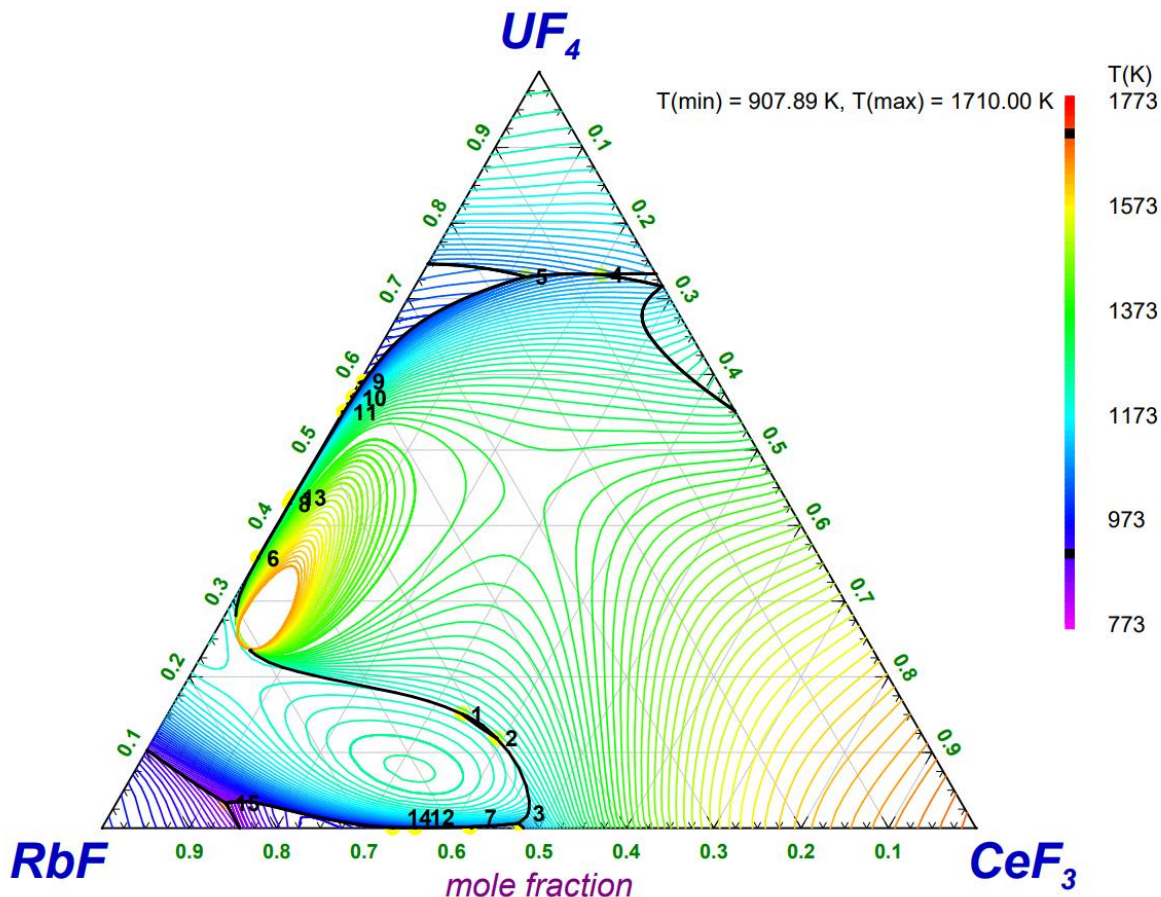


Fig. 6. 9: $\text{RbF-CeF}_3\text{-UF}_4$ ternary phase diagram, four-phase intersection points 1-15 details provided in **Table 7.4**.

6.6.4 The $\text{RbF-PuF}_3\text{-UF}_4$ system

Integrating the sub binary systems RbF-PuF_3 and RbF-UF_4 from the previous chapters, and the newly optimised $\text{PuF}_3\text{-UF}_4$ system in this chapter enable the ternary system $\text{RbF-PuF}_3\text{-UF}_4$ to be calculated in this work.

The ternary phase diagram with all four-phase intersection points with the molten salt solutions are given in **Table 6.5** and **Fig 6.10**:

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Table 6. 5: Four-phase equilibria intersection points in the RbF-PuF₃-UF₄ system

No.	X (UF ₄)	X (RbF)	X (PuF ₃)	T (K)	Equilibrium	Solid phases in equilibria
1	0.22302	0.65605	0.12092	1227.40	Eutectic	(Pu, U)F _x (s.s.), RbPu ₂ F ₇ , Rb ₃ UF ₇
2	0.19915	0.54402	0.25683	1222.35	Eutectic	(Pu, U)F _x (s.s.), Rb ₂ UF ₆ , Rb ₃ UF ₇
3	0.08517	0.45488	0.45635	1213.78	Peritectic	Rb ₂ UF ₆ (s2), (Pu, U)F _x (s.s.), Rb ₃ UF ₇
4	0.31693	0.67962	0.00345	1191.21	Peritectic	RbPu ₂ F ₇ (s2), (Pu, U)F _x (s.s.), Rb ₃ UF ₇
5	0.02195	0.4787	0.49935	1167.01	Peritectic	RbPu ₂ F ₇ (s2), (Pu, U)F _x (s.s.), Rb ₃ UF ₇
6	0.72336	0.08844	0.1882	1117.91	Peritectic	UF ₄ , PuU ₂ F ₁₁ , (Pu, U)F _x (s.s.)
7	0.00312	0.54467	0.45222	1103.03	Peritectic	RbPu ₂ F ₇ (s1), RbPu ₂ F ₇ (s2), Rb ₃ UF ₇
8	0.72202	0.13424	0.14374	1099.21	Peritectic	UF ₄ , (Pu, U)F _x (s.s.), RbU ₆ F ₂₅
9	0.35695	0.64275	0.0003	1079.60	Peritectic	(Pu, U)F _x (s.s.), Rb ₂ UF ₆ , Rb ₃ UF ₇
10	0.59087	0.40198	0.00715	1040.38	Peritectic	(Pu, U)F _x (s.s.), RbU ₃ F ₁₃ , RbU ₆ F ₂₅
11	0.00045	0.61231	0.38724	994.78	Eutectic	RbPu ₂ F ₇ (s1), PuUF ₄ , Rb ₃ UF ₇
12	0.56888	0.42656	0.00456	988.34	Peritectic	(Pu, U)F _x (s.s.), Rb ₂ U ₃ F ₁₄ , RbU ₃ F ₁₃
13	0.55025	0.44656	0.00319	982.70	Eutectic	(Pu, U)F _x (s.s.), Rb ₂ U ₃ F ₁₄ , RbUF ₅
14	0.43664	0.56309	0.00027	960.82	Peritectic	(Pu, U)F _x (s.s.), Rb ₆ U ₇ F ₃₁ , RbUF ₅
15	0.42957	0.57023	0.0002	950.90	Eutectic	(Pu, U)F _x (s.s.), Rb ₆ U ₇ F ₃₁ , Rb ₂ UF ₆
16	0.00058	0.66808	0.33134	945.00	Eutectic	Rb ₃ PuF ₇ , RbPuF ₄ , Rb ₃ UF ₇
17	0.03041	0.83965	0.12995	903.57	Eutectic	RbF, Rb ₃ PuF ₆ , Rb ₃ UF ₇

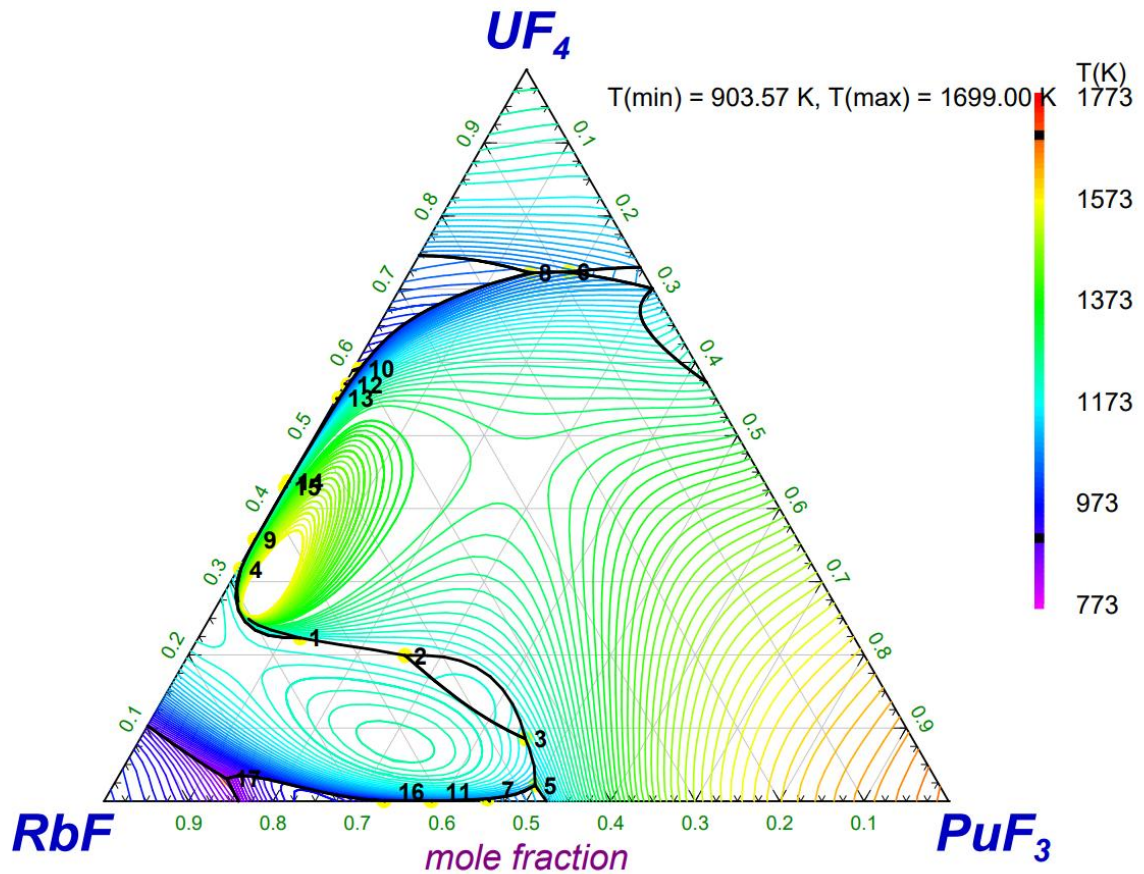
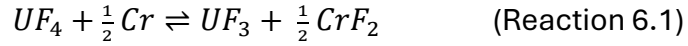


Fig. 6. 10: $\text{RbF-PuF}_3\text{-UF}_4$ ternary phase diagram, four-phase intersection points 1-15 details provided in **Table 6.5**.

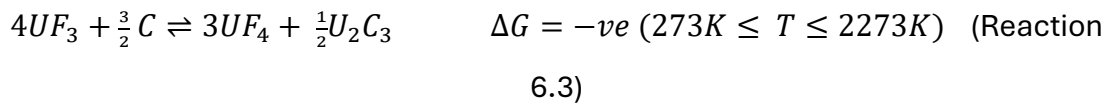
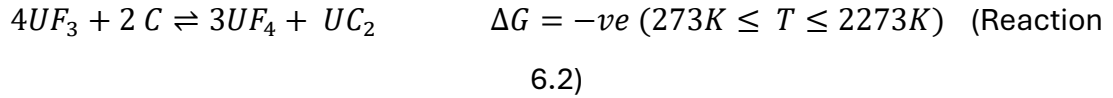
6.6.5 Redox control, corrosion mitigation and tellurium embrittlement

As outlined in Chapters 2-4, corrosion in molten salt reactors (MSRs) is fundamentally governed by Gibbs free energy gradients arising from thermally induced differences in chemical potential [75]. In the Molten Salt Reactor Experiment (MSRE), researchers at Oak Ridge National Laboratory (ORNL) demonstrated that careful control of the redox potential was essential for mitigating alloy corrosion, leading to the adoption of high-nickel alloys such as Hastelloy-N in place of chromium-bearing stainless steels [78].

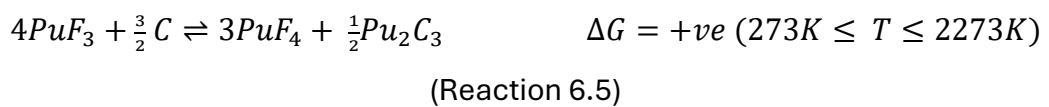
This approach relied on shifting the $\text{U}^{4+}/\text{U}^{3+}$ ratio in the $\text{LiF-BeF}_2\text{-ZrF}_4\text{-UF}_4$ fuel salt toward more reducing conditions by increasing U^{3+} content by increasing UF_3/UF_4 ratio, effectively suppressing chromium leaching. This is caused by the oxidative properties of UF_4 , demonstrated by **reaction 6.1**:



Previous researchers [23] also noted that with too high UF₃/UF₄ ratio, can make the fuel salt too reducing, which was experimentally observed with an increase of uranium carbide formation on the surfaces of the graphite moderator within the MSRE core from the following reactions 2-3 due to UF₃ having a far lower redox potential (also seen in **Fig. 20**):



Heavier and larger alkali cations such as Rb⁺, present in RbF, promote stronger complex formation with UF₄, producing a more negative Gibbs free energy in the liquid binary system. Consequently, the activity of UF₄ within the melt decreases, while the activity of the [UF_x]ⁿ⁻ complexes increases due to their greater thermodynamic stability. Although the proposed hypothesis is preliminary and open to evaluation, it is further supported by the results from this thermodynamic assessment carried out in this chapter, shown in **Fig. 6.11**, where the addition of RbF significantly lowers the Gibbs energy and thus lowering the redox potential compared to FLiBe-based UF₄ fuel salt, making chromium leaching far less thermodynamically favourable. A particularly interesting aspect is that this reintroduces the possibility of reducing the redox potential of the fuel salt without the addition of UF₃, while still maintaining conditions that are also thermodynamically unfavourable for uranium carbide formation via the pathways illustrated in reactions 2 and 3.



Chapter 6: Thermodynamic investigation of the CeF_3 - UF_4 system and the RbF - MF_3 - UF_4 systems ($\text{M} = \text{Ce}, \text{Pu}$)

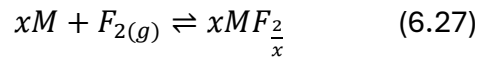
Similarly, PuF_3 , with similar properties to UF_3 would be expected to form analogous carbides as described in Reactions 6.4 & 6.5. Using thermodynamic data from Gurvich [68], interestingly, the Gibbs energy change of plutonium carbides formation is positive across all MSR-relevant temperatures. Additionally, CeF_3 has been experimentally shown to form stable $[\text{MF}_6]^{3-}$ complexes in RbF solutions, and PuF_3 is expected to exhibit analogous complexation behaviour due to its close chemical similarity, resulting in similarly more negative Gibbs energies within the binary systems. This mechanism would, in theory, further suppress the thermodynamic propensity for plutonium carbide formation at the graphite moderator interface.

It not properly understood the exact mechanisms of the variations in the oxidation state between the $\text{U}^{3+} / \text{U}^{4+}$ within a molten UF_3/UF_4 fluoride salt solution, and it may be possible that the change in oxidation state of $\text{Pu}^{3+} / \text{U}^{4+}$ conversion with a PuF_3/UF_4 solution is similar, due to chemical difference between Pu and U . Enriched LiF and BeF_2 may have superior neutronics, having very low neutron absorption cross-section – which is most important for a high performance $^{232}\text{Th}/^{233}\text{U}$ thermal breeder MSR where excess neutrons from thermal based fission are low. However, Toth et al. (1995) [111] noted there was a trade-off made with LiF - BeF_2 mix, having a very low temperature eutectic melting point at $\text{LiF} = 48 \text{ mol\%}$, $\text{BeF}_2 = 52 \text{ mol\%}$ at 633 K, however, at this composition, $-\text{BeF}_4^-$ bridging occurred which drastically increased viscosity of the melt. It was found that 2:1 $\text{LiF} : \text{BeF}_2$ was the best compromise as there was ample fluorine supply to support formation of $[\text{BeF}_4]^-$ without bridging the F . That said, the comprised composition including UF_4 , the combined enthalpy of mixing of these components results in a less negative total Gibbs energy of the ternary LiF - BeF_2 - UF_4 system.

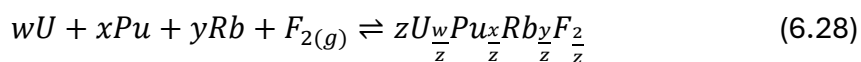
The enthalpy of mixing – although not the only thermodynamic parameter – is significant and contributes largely to the total Gibbs energy of a molten salt solution. Using heavier and larger cationic KF and RbF salts in binary systems with ZrF_4 , ThF_4 , UF_4 have far more negative total Gibbs energies than with lighter carrier salts such as LiF and BeF_2 . A thermodynamic assessment of the original MSRE fuel system (LiF - BeF_2 - ZrF_4 - UF_4) has been completed by Beneš et al. (2008) [135]. The

thermodynamic properties were applied in the FactSage 8.3, and a quick analysis of the enthalpy of mixing terms in several of the sub-binary systems were significantly non-zero near the end members, which is thermodynamically inconsistent. For this reason, Beneš' work was not used in this chapter, as it would have yielded thermodynamically incorrect results. Capelli et al. (2015) [162] remodelled the LiF-BeF₂-UF₄ system with far more consistent results so the data from this publication was used instead. Shown in **Fig. 6.11**, the completed thermodynamic assessment from Capelli et al. (2015) [162] of the two ternary eutectics in LiF-BeF₂-UF₄ systems are plotted in an Ellingham diagram along with the RbF-PuF₃-UF₄ system from this work. It is seen that LiF-BeF₂-UF₄ ternary eutectics have a higher redox potential – therefore it can be realised to be more oxidising due to its less negative total Gibbs energy. To help highlight this point, the second ternary eutectic, 'LiF-BeF₂-UF₄ (2)', is only slightly more reducing than pure UF₄ – the most oxidising component of an MSR starting fuel. In the MSRE, very small amount of UF₃ were added to the UF₄ to make their salt chemistry more reducing to decelerate **Reaction 1** from stripping Cr from the alloy into fluoride salt solution. A viable alternative as a pathway forward developing MSR fuel to include heavier and larger AlkF salts to make the fuel salt far more reducing without any addition of UF₃.

An Ellingham diagram is used here to illustrate the Gibbs free energy changes of reactions between alloying components and various salts as a function of temperature. The Gibbs free energy change of these formation reactions per mol of F₂ (g) can be simplified as:



Where x is the stoichiometric coefficient to balance the reaction per mole of pure F₂ gas, M is metal element (M = Mo, Ni, Fe, Cr, Mn, U, Pu, Rb) of the fuel or alloy component. Or in the case of the formation of the ternary molten salt solution in this work:



Where y and z are additional stoichiometric coefficients to balance the reaction per mole of pure F₂ gas for the RbF-PuF₃-UF₄ solution.

The Gibbs free energy of the forward reaction per mole of F₂(g) in Equation 6.27 can then be written as:

$$\Delta G_r^\circ = xG_{MF_2}^\circ - \left(xG_M^\circ + xG_{F_2(g)}^\circ \right) \quad (6.29)$$

Similarly for Equation 28, the Gibbs free energy of the forward reaction per mole of F₂(g) for the RbF-PuF₃ solution:

$$\Delta G_r^\circ = zG_{U_wPu_xRb_yF_2}^\circ - \left(wG_U^\circ + xG_{Pu}^\circ + yG_{Rb}^\circ + xG_{F_2(g)}^\circ \right) \quad (6.30)$$

In this work, the newly modelled RbF-PuF₃-UF₄ system, two ternary eutectics redox potentials are plotted against other pure salts components including alloy corrosion products in **Fig. 6.11**:

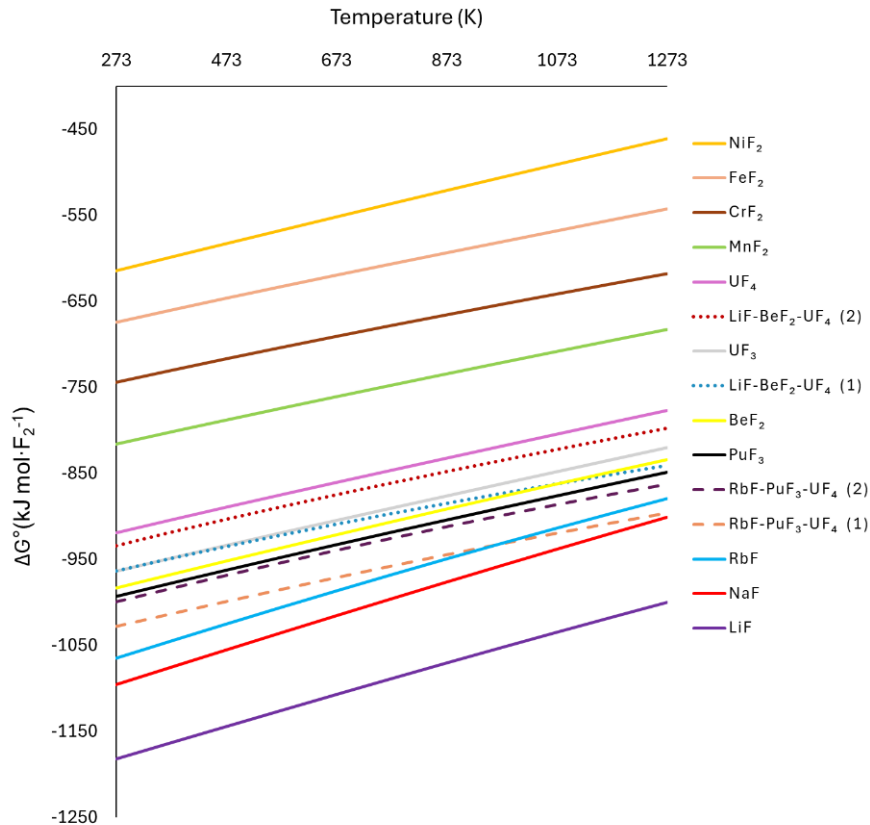


Fig. 6. 1: Standard Gibbs free energy of formation per mole of F₂ for salt components, corrosion products and molten salt solution ternary eutectic; RbF-PuF₃-UF₄ (1) = 83.965 mol% RbF – 12.995 mol% PuF₃ – 3.041 mol% UF₄ and second

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eutectic; $\text{RbF-PuF}_3\text{-UF}_4$ (2) = 54.402 mol% RbF – 25.683 mol% PuF_3 – 19.915 mol% UF_4 modelled in this work. $\text{LiF-BeF}_2\text{-UF}_4$ (1) is ternary eutectic taken from Capelli et al. (2015) [162] thermodynamic assessment with composition 8.35 mol% LiF – 68.68 mol% BeF_2 – 22.98 mol% UF_4 . The second ternary eutectic in Capelli et al. [162] $\text{LiF-BeF}_2\text{-UF}_4$ (2) with composition 11.2 mol% LiF – 47.9 mol% BeF_2 – 50.99 mol% UF_4 is also plotted. Other data from Gurvich [68].

Tellurium cracking was another notable challenge experienced in the MSRE. The chemistry and the thermodynamic processes of the fission product tellurium was never fully understood, mainly because of its complex chemistry and ability to exist in many oxidation states (e.g. Te^{-2} , Te^{-1} , Te^0 , Te^{+2} , Te^{+4} , Te^{+6}). McCoy (1978) [22] reviews this in detail from the experience gathered from the MSRE. Numerous experiments were conducted to investigate the precise mechanism by which tellurium forms compounds with the primary alloying element, nickel, in Hastelloy-N used in the MSRE. It was found that Te species did not react and diffuse directly onto the Hastelloy-N exposed surfaces, e.g. forming uniform a Ni_3Te_2 layer, but rather accumulate at Te rich regions along grain boundaries at concentrations high enough to form intermediate Ni_xTe_y compounds leading to intergranular embrittlement.

One of the key findings from Keiser (1977) [77] was Hastelloy N showed no signs of tellurium-induced embrittlement when exposed to a vapor atmosphere generated from $\text{Ni}_3\text{Te}_2 + \text{Ni}$. In contrast, when Hastelloy N was exposed to molten $\text{LiF-BeF}_2\text{-ThF}_4$ salt containing $\text{Ni}_3\text{Te}_2 + \text{Ni}$, extensive intergranular cracking was observed. It was quickly established that the molten salt solution was vital for interfering with the chemistry, making Te more anionic in that it forms a compound with Ni. Other suggestions by McCoy (1978) [22] were made such as adding CrF_2 in the hope that Cr_xTe_y compounds were formed preferentially instead of the alloying MSRE components, but no strong conclusions were drawn.

McCoy [22] reviewed the effects of titanium modification on Hastelloy N, reporting that 2 wt% Ti additions reduced, but did not entirely prevent tellurium-induced intergranular cracking. The remaining susceptibility was attributed to insufficient hot ductility to accommodate residual stresses from prior working and annealing operations. The Ti-modified alloy also exhibited lower corrosion in molten salt,

partly due to its reduced iron content compared to conventional Hastelloy N. Although titanium, like iron, readily forms fluorides in the molten salt environment, its diffusion rate to the alloy surface is an order of magnitude (or more) slower than that of chromium, which contributes significantly to the reduced corrosion rate. Further alloying with niobium improved resistance to tellurium embrittlement, though only up to a limiting concentration of approximately 1-2 wt% Nb.

Kieser (1977) [77] demonstrated that controlling the redox state of the fuel salt had the most pronounced effect in mitigating tellurium-induced embrittlement. Severe cracking occurred when the UF_4/UF_3 ratio exceeded 80, whereas a ratio of 60 or lower resulted in markedly reduced embrittlement. This relationship of UF_4/UF_3 ratio and Te cracking is illustrated clearly in Fig. 6.12.

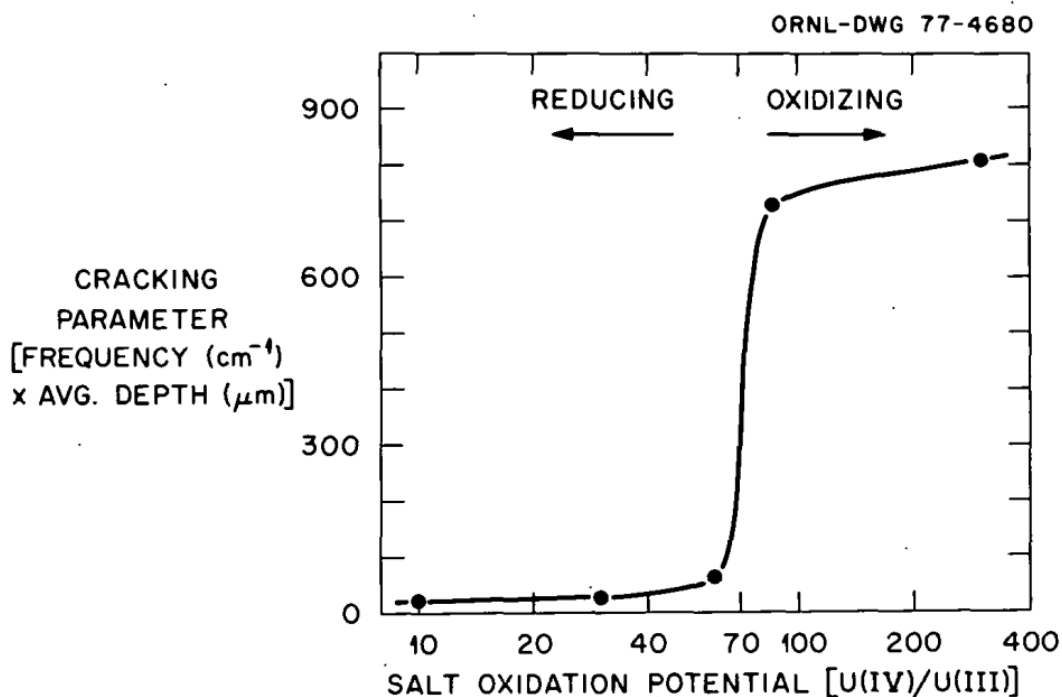


Fig. 6. 12: Cracking behaviour of Hastelloy N exposed 260 hr at 973 K in LiF - BeF_2 - ThF_4 salt containing CrTe1.266 as a Te source [77].

Importantly, these experiments were conducted in LiF - BeF_2 - ThF_4 salt mixtures, which are themselves not highly reducing, owing to their relatively less negative Gibbs free energy/higher redox potential. Despite this, when the UF_4/UF_3 ratio was reduced below 7 (i.e., $\text{UF}_3 = 14.29$ mol%), no cracking was observed during 260 h exposures at 973 K. This finding underscores that even within a moderately oxidising

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salt system such as $\text{LiF-BeF}_2\text{-ThF}_4$, maintaining sufficiently reducing conditions is critical to completely suppress tellurium-induced degradation.

Prior to Kieser's [77] study, Toth and Gilpatrick (1973) [23] had established a lower practical limit for the UF_4/UF_3 ratio in LiF-BeF_2 mixtures at approximately 10, in order to avoid overly reducing conditions that promote uranium carbide formation on graphite moderators. The chemistry and thermodynamics of molten fuel salts are inherently complex, and further experimental validation is required in this area. Nevertheless, it is plausible that issues such as chromium leaching, uranium carbide formation, and tellurium embrittlement could be simultaneously mitigated by abandoning both the conventional LiF-BeF_2 carrier salt and the use of UF_3 doping for redox control.

An alternative approach would involve employing heavier alkali and alkaline earth fluorides such as KF , RbF , and CaF_2 which provide more negative enthalpies of mixing than LiF or BeF_2 . This would lower the overall Gibbs free energy of the molten mixture and consequently reduce the redox potential without requiring UF_3 additions, the main concern that otherwise risks creating overly reducing conditions conducive to carbide formation. While this hypothesis remains to be verified, it is possible that such heavier carrier salts, in ternary or quaternary systems, may result in higher eutectic melting points compared with LiF-BeF_2 . This highlights an inherent trade-off: corrosion resistance of structural materials may be improved, but at the expense of other physical properties such as melting temperature, viscosity, or heat capacity.

The adoption of LiF-BeF_2 as a carrier salt in historical designs was primarily motivated by its superior neutronic characteristics and suitability for high-performance breeder reactors. However, none of the contemporary MSR concepts (aside from China's TMSR-1) are currently intended to breed ^{233}U from ^{232}Th . This suggests that future research should focus on exploring heavier and larger cation fluoride systems containing UF_4 in ternary and higher-order compositions, to identify formulations with minimal melting points while optimising the most critical thermophysical and chemical properties for each specific MSR design.

Chapter 6: Thermodynamic investigation of the CeF_3 - UF_4 system and the RbF - MF_3 - UF_4 systems ($\text{M} = \text{Ce}, \text{Pu}$)

Previous work at ORNL [80] during the Aircraft Reactor Experiment (ARE) and later reviewed by Kairos and Argonne [81] highlighted the influence of cation–anion size effects, particularly the charge-to-radius (Z/r) ratio, on molten salt thermodynamics. Deviations from ideal solution behaviour often arise from negative heats of mixing, where certain mixed molten salts can be more stable than their pure liquid phase components, and from changes in entropy due to lattice order or disorder when dissimilar cations are combined. For example, researchers [80] experimentally demonstrated in NaF - ZrF_4 mixtures, UF_4 addition suppressed ZrF_4 activity but destabilised UF_4 , demonstrating how Z/r ratios and complexation both drive non-ideal behaviour. They described these systems in terms of “fluoroacidity,” where alkali cations act as fluoride donors and multivalent cations as acceptors, forming complexes such as $[\text{MF}_6]^{3-}$. Rubidium, being more basic than Li^+ or Na^+ , donates fluoride more effectively to Ce^{3+} and Pu^{3+} , stabilising the melt and limiting alloy dissolution. This was also briefly addressed in a later study by Ocádiz-Flores [82] further discussing the idea that lowering Gibbs free energy enhances thermodynamic stability.

These findings suggest that in the ternary RbF - PuF_3 - UF_4 system, the combined presence of Rb , Pu , and U cations, each retaining the complexation behaviour observed in their respective binary subsystems,

A final consideration, not yet discussed, is that the vapor species of a particular molten salt mixture, even at a fixed composition, may exhibit desirable features such as low partial pressure, but they possess thermodynamic properties that differ radically from the liquid phase. These differences could significantly enhance corrosion. Therefore, future studies should investigate vapor-phase behaviour only after the desirable liquid properties have been fully established.

6.7 Conclusion

The RbF - PuF_3 - UF_4 system is a key ternary for assessing RbF -containing plutonium- and uranium-based salts in molten salt reactors (MSRs), as a certain proportion of ^{238}U within the UF_4 fuel component will always undergo neutron capture to ^{239}Pu and

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^{240}Pu under neutron irradiation. In this work, the system is experimentally investigated using CeF_3 as a surrogate and thermodynamically modelled. The modelling accounts for $[\text{UF}_7]^{3-}$, $[\text{UF}_6]^{2-}$, $[\text{UF}_5]^-$, and $[\text{PuF}_6]^{3-}$ complexes in the melt, similar to those identified KF - CeF_3 - and KF - ZrF_4 - based proxy systems via Raman spectroscopy. Each of these species exhibits distinct short-range ordering behaviours at defined compositions, representing a novel advancement in the thermodynamic characterisation of MSR fluoride fuel salts using FactSage software.

The inclusion of multiple complexes within the sub-binary systems improves the robustness of modelling higher-order systems. By contrast, the conventional FactSage approach assigns Gibbs energy functions to the liquid solution as a function of a single end-member composition (e.g. UF_4). Although this method provides speed and convenience for simple systems, such as those with a single eutectic and few intermediate compounds, it has inherent limitations. It models short-range ordering (SRO) at only a single composition, which becomes increasingly inadequate as system complexity grows. Moreover, Raman spectroscopy studies demonstrate that SRO arises from specific complex formation rather than a random distribution of ions in the melt, highlighting the method's limited representativeness. For realistic industrial application to MSR technology, such complexity is unavoidable due to the accumulation of fission products and corrosion components during normal operation. This is corroborated by DSC heating analysis of the RbF - CeF_3 - UF_4 system, where the model predicted a ternary eutectic validated experimentally at 904 K.

Other identified eutectics exhibit relatively high melting temperatures, which are less attractive for reactor operation. However, they maintain largely negative Gibbs energies, potentially improving corrosion resistance. Future quaternary studies incorporating NaF and KF could reduce melting temperatures while preserving desirable thermo-physical and neutronic properties.

The composition $X(\text{RbF}) = 0.83965$, $X(\text{UF}_4) = 0.03041$, and $X(\text{PuF}_3) = 0.12995$ may permit higher plutonium loading or the substitution of UF_3 for PuF_3 due to analogous properties. This could support smaller, more compact MSR cores, reducing the size

of critical components and capital costs. However, **Fig. 6.9** indicates a steep liquidus towards the UF_4 -rich side; even small compositional deviations in the stoichiometry could significantly alter the melting point. Shallow liquidus ternary or higher-order eutectics could offer more consistent melting if mass industrial fabrication of fuel salt was. Another ternary eutectic occurs at $X(\text{RbF}) = 0.54402$, $X(\text{UF}_4) = 0.19915$, and $X(\text{PuF}_3) = 0.25683$; however, its high melting point of 1222.35 K makes it unsuitable for practical applications.

Consequently, $\text{RbF-PuF}_3\text{-UF}_4$ could be promising candidate for advanced fluoride-based fuel salts, while $\text{RbF-CeF}_3\text{-UF}_4$ remains relevant due to Ce as a fission product. The UF_3/UF_4 ratio is frequently discussed in the literature to control redox potential and mitigate corrosion. However, limited attention has been given to systematically evaluating redox potentials across different thermodynamically characterised actinide salt solutions, their compositional variations, and their ability to form thermodynamically stable complexes that reduce dissolution of alloying components. This study addresses this gap using FactSage software and Ellingham diagrams.

This work also demonstrates the importance of robust methods for determining thermodynamic properties in data-scarce systems. Extending Gibbs energy functions to include multi-coordinated plutonium and cerium complexes in sub-binary systems while maintaining reliability for higher-order systems is supported by high-sensitivity DSC with low-mass crucibles. This approach enables efficient modelling with minimal sample consumption and waste. As a study of a ternary salt system, these findings provide a critical foundation for future investigations into ternary and higher-order actinide-containing salts, supporting advanced fuel cycles and next-generation MSR technologies.

Chapter 7: Thermodynamic investigation of the $\text{CeCl}_3\text{-UCl}_4$ system and the $\text{RbCl-MCl}_3\text{-UCl}_4$ systems ($\text{M} = \text{Ce, Pu}$)

7.1 Abstract

This chapter introduces higher-order systems, building on the thermodynamic assessments of binary systems presented in the previous chapters. To obtain the complete thermodynamic description of the $\text{RbCl-CeCl}_3\text{-PuCl}_3\text{-UCl}_4$ system, the final binary interaction $\text{PuCl}_3\text{-UCl}_4$ was evaluated using $\text{CeCl}_3\text{-UCl}_4$ as a surrogate, supported by novel DSC analysis to confirm the eutectic temperature. The two ternary systems $\text{RbCl-CeCl}_3\text{-UCl}_4$ and $\text{RbCl-PuCl}_3\text{-UCl}_4$ have been assessed for the first time. The ternary systems exhibit multiple eutectics, some of which present promising compositions in terms of fissile concentration and operating temperature. Thermodynamic modelling was performed using Factsage, employing the CALPHAD method in combination with the MQMQA (modified quasi-chemical model with quadruplet approximation), which retains the various plutonium- and uranium-coordinated complexes identified in the RbCl-CeCl_3 , RbCl-PuCl_3 and RbCl-UCl_4 binary system. By introducing Gibbs energy functions for specific complexes rather than relying solely on broad end-member components, the reliability of the model is improved as the system expands in both components and complexity.

7.2 Introduction

Molten salt reactors (MSRs) are one of the chosen Gen-IV nuclear reactor designs that continues to see vast support, research and development across a span of various private companies and federal-level government globally. Out of the Gen-IV designs, which include a variety of different and exotic fuels and coolants, MSRs are the only reactor concept that relies on the fuel being completely liquid. Rather than liquid metal fuels – which was also explored historically – would not yield the same advantage of having a liquid phase that has ionic properties, allowing larger safety benefits to be adopted, such as, and the main one being fission-product solubility.

Having a nuclear fuel in a liquid phase than a solid fuel which is uniform in phase like UO_2 , although can be more complex to predict its properties and model, therefore requiring rigorous experimental investigation and validation, allows for far more inherent safety features. Unlike solid-fuel reactors, which are constrained by fixed geometry and mechanical control structures, MSR offers significant design flexibility and configurational freedom, enabling a wide spectrum of reactor architectures. This is highlighted in the IAEA 2023 Status of MSR Technology report [26], where there are 4 main classifications; graphite based, homogeneous, heterogeneous and 'other types' where specific design would struggle to fit under the previous three. Other notable historical works by Taube at the Swiss nuclear institute also highlighted that MSRs could be designed specifically for various main purposes, i.e. for maximum electricity production, for direct heating applications or for long-term sustainability and energy security as breeder type reactors [16].

With the wide range of MSR classifications and applications, fuel selection is a central priority, as it defines the thermo-physical, chemical, and neutronic property limits that ultimately shape the entire reactor design. The choice of fuel salt must satisfy not only these performance requirements but also regulatory standards to ensure safety. Key criteria include: an appropriate melting point, sufficient solubility of actinide components, and the ability to retain fission products either in solution or as thermally stable compounds. Additional desirable traits are high heat capacity and thermal conductivity, low vapor pressure with a high boiling point, adequate density to sustain fission, low viscosity, strong resistance to neutron irradiation and corrosion, and a controllable redox potential.

In the literature, prior focus on fluoride fuel salt were inclusive of the lighter alkali-metal fluoride (AlkCl) containing mixtures, such as LiCl or NaCl . While LiCl-UCl_4 binary system exhibits some desirable traits such as simpler phase diagrams with one eutectic and lower melting temperatures than heavier AlkCl containing binary systems, the one eutectic offers less degrees of freedom in design and subsequently for LiCl containing higher order systems. The enthalpy of mixing for such systems, plays a main contributing factor into the total Gibbs energy of the mixed system, and therefore the thermal stability of the final mixed solution. Less

explored are the heavier AlkCl containing systems such as KCl and RbCl . In this work, we continue the focus on the RbF containing systems from previous chapters, for the novel thermal assessments, yet whilst also providing a benchmark for future works.

Building on from the binary fluoride systems in previous chapters, unexplored ternary systems $\text{RbCl-CeCl}_3\text{-UCl}_4$ and $\text{RbCl-PuCl}_3\text{-UCl}_4$ will be assessed and completed using Calculation of Phase Diagram (CALPHAD) technique with Factsage software version 8.3. These ternary systems have not yet been reported or assessed in the literature. The investigated system demonstrates considerable compositional flexibility at operating temperatures, which may prove advantageous in meeting requirements for other essential fuel properties. Furthermore, the Gibbs energy-based model developed in this chapter can be applied to construct Ellingham diagrams, enabling the evaluation of the salt's redox potential and illustrating the corresponding corrosion tendencies at any selected molten salt composition providing that other attractive characteristics are met, i.e. melting point, fissile component concentration and neutronics.

7.3 Crystallography

Crystallographic data are fundamental for understanding both the structural and physical properties of compounds. These data reveal atomic arrangements, space groups, and lattice parameters, which are essential for evaluating phase diagrams. Documenting such structures is particularly important, as the future development of higher-order systems containing $\text{RbCl-CeCl}_3\text{-PuCl}_3\text{-UCl}_4$ binary components may yield intermediate compounds with comparable crystal structures. In cases where structurally compatible phases emerge, their shared crystallography could facilitate interstitial or substitutional cation exchange within a common sublattice. This mechanism would allow continuous solid solutions to form, rather than distinct and separate solid phases.

Table 7. 1: Summary of the crystallographic data of intermediate solid compounds in the RbF-CeCl₃-PuCl₃-UCl₄ system

Fluoride	Space group	ρ (g cm ⁻³)	Ref.
RbCl	$Fm\bar{3}m^*$	3.05	[165]
UCl ₄	$I4_1/amd$	6.02	[95]
CeCl ₃	$P21/m$	3.95	[53]
PuCl ₃	$P21/m$	5.97	[54]
(Ce, U)Cl _x (s.s.)	$I4_1/amd$	n/a	-
(Pu, U)Cl _x (s.s.)	$I4_1/amd$	n/a	-
Rb ₂ UCl ₆	$C2/m$	3.76	[95]
RbUCl ₅	n/a	n/a	-
Rb ₃ CeCl ₆ (s1)	$Fm3m$	2.50	[51]
Rb ₃ CeCl ₆ (s2)	n/a	n/a	-
RbCeCl ₅	$Pnma$	3.36	[52]
RbCe ₂ Cl ₇ (s1)	$P21/n$	n/a	-
RbCe ₂ Cl ₇ (s1)	n/a	n/a	-

Table 7.1 summarizes the data available for both the end members and the intermediate compounds studied. Previously highlighted in chapters intermediate compounds of this RbCl-PuCl₃ system are assumed to have the same crystallography as the intermediate RbCl-CeCl₃ system. This strongly suggests that, within the two broader RbCl-CeCl₃-UCl₄ and RbCl-PuCl₃-UCl₄ ternary systems under the study of this chapter, the likelihood of interstitial or substitutional cation exchange within a common sublattice will be minimal or absent.

7.4 Thermodynamic Modelling

The thermodynamic models presented in this work were developed using FactSage software (version 8.3) and manual iterative techniques, within the framework of the CALPHAD (CALculation of PHase Diagrams) methodology. Optimisation of the Gibbs energy function parameters for all phases in the systems was carried out

using available phase diagram and mixing enthalpy data. Data from previous chapter optimising the RbCl-MCl₃ (where M = Ce, Pu) binary systems and the RbCl-UCl₄ binary system were used, but in this chapter, to complete the ternary systems RbCl-MCl₃-UCl₄, the MCl₃-UCl₄ binary systems are assessed.

7.4.1 Thermodynamics of Pure Compounds

The thermodynamic data ($\Delta H_{298.15K}^{\circ}$, $S_{298.15K}^{\circ}$ and C_P) for all compounds are optimised in this work and are given in **Table 7.2**. The molar Gibbs free energies of these compounds are expressed as:

$$G(T) = \Delta H_{298.15K}^{\circ} - T \cdot S_{298.15K}^{\circ} + \int_{298.15K}^T C_P dT - T \int_{298.15K}^T \frac{C_P}{T} dT \quad (7.1)$$

Where $\Delta H_{298.15K}^{\circ}$ is the standard enthalpy of formation, $S_{298.15K}^{\circ}$ is the standard entropy of formation at 298.15K and C_P represents the isobaric heat capacity. To be consistent with NIST-JANAF, the standard state pressure refers to 1 bar.

As explained in the preceding RbCl-UCl₄ and RbCl-MCl₃ (M = Ce, Pu) chapter, this study, standard RbCl, UCl₄, CeCl₃ and PuCl₃ data from Gurvich [68] are adopted instead. Neumann-Kopp rule was employed to calculate C_P functions of intermediate compounds to ensure physically realistic behaviour. The thermodynamic properties of RbCl-CeCl₃-PuCl₃-UCl₄ end-members and intermediate compounds (**Table 7.2**) were then refined using a manual iterative CALPHAD approach.

Novel CeCl₃-UCl₄ DSC data also suggests there are no stable intermediate compounds in this system, rather a solid solution of CeCl₃ in UCl₄, therefore, due to the high analogous nature of CeCl₃ to PuCl₃, the solid solution on PuCl₃ in UCl₄ was modelled using the same parameters for consistency.

Table 7. 2: Thermodynamic data of the end-member RbCl-CeCl₃-PuCl₃-UCl₄ and their intermediate compounds.

Compound	T range (K)	$\Delta H_{298.15K}^{\circ}$ (J·mol ⁻¹)	$S_{298.15K}^{\circ}$ (J·K ⁻¹ ·mol ⁻¹)	$C_{p,m} = a + b \cdot T + c \cdot T^{-2} + d \cdot T^2$				Ref
				a	b	c	d	
RbCl (s)	298.15 – 1500	435220.0	95.23	48.51268	0.01256576	95.11015	-3.80492E-9	I. Barin (1977)[44]
	1500 - 2400			25.05421037	0.037889418	5533098.364	-7.55943E-6	

Chapter 7: Thermodynamic investigation of the $\text{CeCl}_3\text{-UCl}_4$ system and the $\text{RbCl-MCl}_3\text{-UCl}_4$ systems ($\text{M} = \text{Ce, Pu}$)

	2400 - 3400			73.4				
RbCl (l)	298.15 - 3400	-422526.77	98.44	73.4				I. Barin (1977) [44]
CeCl ₃ (s)	298.15 - 1400	-1059700	151.42	90.9772	0.0358123	-271530		I. Barin (1977) [44]
	1400 - 2300			23.8740662	0.109906341	14156259.31	-2.23758E-5	
	2300 - 3400			161.05				
CeCl ₃ (l)	298.15 - 3000	-1042566.19	136.70	161.05				I. Barin (1977) [44]
PuCl ₃ (s)	298.15 - 1040	-959600.00	161.70	91.35	0.024	240000		Gurvltch (1994) [68]
	1040 - 1450			144.1391155	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			122.15252				
PuCl ₃ (l)	298.15 - 1040	-904600.01	214.53	91.35	0.024	240000		Gurvltch (1994)[68]
	1040 - 1500			145				
UCl ₄ (s)	298.15- 1100	-1019201.0	197.10	109.8	-0.0405			Gurvltch (1994)[68]
	1100-2500			154.35				
UCl ₄ (s)	298.15-650	-976372.706	246.277	109/.8	-0.0405			
	650-1200			107.9	-0.06025			
	1200-3000			180/2				
Rb ₃ CeCl ₆ (α)	298.15 - 1400	-2397771.156	468.86	236.51524	0.07350958	-271244.66955	-1.141476E-8	This work
	1400 - 1500			169.41210622	0.147603621	14156544.64045	-2.238721476E-5	
	1500 - 2300			99.03669733	0.223574595	30755554.402	-4.505409E-5	
	2300 - 2400			236.21263111	0.113668254	16599295.092	-2.267829E-5	
	2400 - 3000			381.25				
Rb ₃ CeCl ₆ (β)	298.15 - 1400	-2389251.406	482.11	236.51524	0.07350958	-271244.66955	-1.141476E-8	This work
	1400 - 1500			169.41210622	0.147603621	14156544.64045	-2.238721476E-5	
	1500 - 2300			99.03669733	0.223574595	30755554.402	-4.505409E-5	
	2300 - 2400			236.21263111	0.113668254	16599295.092	-2.267829E-5	
	2400 - 3000			381.25				
Rb ₂ CeCl ₅	298.15 - 1400	-1951115.367	371.88	188.00256	0.06094382	-271339.7797	-7.60984E-9	This work
	1400 - 1500			120.89942622	0.135037861	1415 6449.5303	-2.238340984E-5	
	1500 - 2300			73.98248696	0.185685177	25222456.038	-3.749466E-5	
	2300 - 2400			211.15842074	0.075778836	11066196.728	-1.511886E-5	
	2400 - 3000			307.85				
RbCe ₂ Cl ₇ (α)	298.15 - 1400	-2565230.59	426.07	230.46708	0.08419036	-542964.88985	-3.80492E-9	This work
	1400 - 1500			96.26081244	0.232378442	28312613.73015	-4.475540492E-5	
	1500 - 2300			72.80234281	0.2577021	33845616.984	-5.231103E-5	
	2300 - 2400			347.15421037	0.037889418	5533098. 364	-7.55943E-6	
	2400 - 3000			395.5				
RbCe ₂ Cl ₇ (β)	298.15 - 1400	-2563874.59	428.07	230.46708	0.08419036	-542964.88985	-3.80492E-9	This work
	1400 - 1500			96.26081244	0.232378442	28312613.73015	-4.475540492E-5	
	1500 - 2300			72.80234281	0.2577021	33845616.984	-5.231103E-5	
	2300 - 2400			347.15421037	0.037889418	553 3098.364	-7.55943E-6	
	2400 - 3000			395.5				
PuCl ₃ (s)	298.15 - 1040	-959600.00	161.70	91.35	0.024	240000		Gurvltch (1994) [68]

Chapter 7: Thermodynamic investigation of the $\text{CeCl}_3\text{-UCl}_4$ system and the $\text{RbCl-MCl}_3\text{-UCl}_4$ systems ($\text{M} = \text{Ce, Pu}$)

	1040 – 1450			144.1391155	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			122.15252				
$\text{PuCl}_3(\text{l})$	298.15 - 1040	-904600.01	214.53	91.35	0.024	240000		Gurvich (1994)[68]
	1040 - 1500			145				
$\text{Rb}_2\text{PuCl}_6(\alpha)$	298.15 - 950	-2276435.75	500.00	236.88804	0.06169728	240285.33045	-1.141476E-8	This work
	950 – 1040			192.8153391	0.150270903	2214743.742	-4.68567E-5	
	1040 – 1328			245.6044546	0.121016221	-19722461.068	-4.87948E-5	
	1328 – 1450			331.77606064	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			309.78946514				
$\text{Rb}_2\text{PuCl}_6(\beta)$	298.15 - 950	-2258314.70	527.00	236.88804	0.06169728	240285.33045	-1.141476E-8	This work
	950 – 1040			192.8153391	0.150270903	2214743.742	-4.68567E-5	
	1040 – 1328			245.6044546	0.121016221	-19722461.068	-4.87948E-5	
	1328 – 1450			331.77606064	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			309.78946514				
Rb_2PuCl_6	298.15 - 950	-1845919.429	386.80	188.37536	0.04913152	240190.2203	-7.60984E-9	This work
	950 – 1040			158.9935594	0.108180602	1556495.828	-3.12378E-5	
	1040 – 1328			211.7826749	0.07892592	-20380708.982	-3.31759E-5	
	1328 – 1450			269.23041226	-0.005254682	-21697204.81	-1.9381E-6	
	1450 - 2000			247.24381676				
$\text{RbPu}_2\text{Cl}_7(\alpha)$	298.15 - 950	-2358182.464	451.63	231.21268	0.06056576	480095.11015	-3.80492E-9	This work
	950 – 1040			216.5217797	0.090090301	1138247.914	-1.56189E-5	
	1040 – 1328			322.1000107	0.031580937	-42736161.706	-1.94951E-5	
	1328 – 1450			350.82387938	-0.010509364	-43394409.62	-3.8762E-6	
	1450 - 2000			306.85068838				
$\text{RbPu}_2\text{Cl}_7(\beta)$	298.15 - 950	-23504416.664	463.63	231.21268	0.06056576	480095.11015	-3.80492E-9	This work
	950 – 1040			216.5217797	0.090090301	1138247.914	-1.56189E-5	
	1040 – 1328			322.1000107	0.031580937	-42736161.706	-1.94951E-5	
	1328 – 1450			350.82387938	-0.010509364	-43394409.62	-3.8762E-6	
	1450 - 2000			306.85068838				
$\text{Rb}_2\text{UCl}_6(\text{s})$	298.15- 1100	1988433.202	386.56	206.82536	0.06563152	190.2203	-7.60984E-9	This work
	1100-1500			251.37536	0.02513152	190.2203	-7.60984E-9	
	1500-2400			204.45842074	0.075778836	11066196.728	-1.511886E-5	
	2400-3400			301.15				
$\text{RbUCl}_6(\text{s})$	298.15- 1100	1513044.114	280.33	158.31268	0.05306576	95.11015	- 3.80492E-9	This work
	1100-1500			202.86268	0.01256576	95.11015	- 3.80492E-9	
	1500-2400			179.40421037	0.037889418	5533098.364	- 7.55943E-6	
	2400-3400			227.75				

^aLiquid uranium tetrachloride is modelled as an U^{4+}_v , U^{4+}_{vl} and U^{4+}_{vll} mixture, with $g^0_{\text{U}^{4+}_v\text{Cl}_4} = g^0_{\text{UCl}_4} + 0.24207 \cdot (T/K)$, $g^0_{\text{U}^{4+}_{vl}\text{F}_4} = g^0_{\text{UF}_4} + 30.24207 \cdot (T/K)$ and $g^0_{\text{U}^{4+}_{vll}\text{Cl}_4} = g^0_{\text{UCl}_4} + 50.24207 \cdot (T/K)$

7.4.2 Solid Solution Modelling

The Compound Energy Formalism (CEF) is a mathematical formalism, which is often used to describe the thermodynamic properties of solutions that are modelled with sublattice within a mixed solution phase. In this work, the thermodynamic properties of solid solution phases of the fluoride salts are described using the CEF.

Lanthanide and actinide tri and tetra valent halide salts tend to form complex solid solutions. These solid solutions can be considered to consist of sublattices, with one sublattice containing a cation or vacancy, such as U⁴⁺, M³⁺ and the other sublattice containing a vacancy or chloride anion, such as Cl⁻ or Va⁰ – with the vacancy being electro-neutral having no charge.

Noted that THCl₄ PuCl₃ solid solution structures contain no interstitial sites on the cation sublattice, vacancies exist on the anion side, into which Cl⁻ anions can migrate. In contrast to other studies that treat M³⁺ and Ac⁴⁺ (where M = Pu³⁺, U³⁺, Ac = Th⁴⁺, U⁴⁺) as undergoing simple substitutional reactions, this work employs the compound energy formalism to explicitly integrate these vacancies, Va⁰ on the anion sublattice. The (MU)Cl phase is thermodynamically treated as (M³⁺, U⁴⁺)₂ (Cl⁻, Va⁰)₂, (where M = Ce, Pu in this work) and its Gibbs energy function per mole is given by the following equation:

$$G_m^{MF_3SS} = y_{M^{3+}}^C \cdot {}^0G_{M^{3+}:Cl^-}^{UCl_4SS} + y_{U^{4+}}^C \cdot {}^0G_{U^{4+}:Cl^-}^{UCl_4SS} + y_{M^{3+}}^C \cdot {}^0G_{M^{3+}:Va^0}^{UCl_4SS} + y_{U^{4+}}^C \cdot {}^0G_{U^{4+}:Va^0}^{UCl_4SS} + RT[y_{M^{3+}} \cdot \ln(y_{M^{3+}}) + y_{U^{4+}} \cdot \ln(y_{U^{4+}}) + y_{Va} \cdot \ln(y_{Va}) + y_{Cl^-} \cdot \ln(y_{Cl^-})] + G^E \quad (7.2)$$

where ${}^0G_{M^{3+}:Cl^-}^{MF_3SS}$, ${}^0G_{U^{4+}:Cl^-}^{MF_3SS}$, ${}^0G_{M^{3+}:Va^0}^{MF_3SS}$ and ${}^0G_{U^{4+}:Va^0}^{MF_3SS}$ refers to the respective standard Gibbs energies of (M³⁺)₁(Cl⁻)₄, (U⁴⁺)₁(Cl⁻)₄, (M³⁺)₁(Va⁰)₄, and (U⁴⁺)₁(Va⁰)₄, pure component end-members (highlighted in **Fig. 7.1**), $y_{M^{3+}}^C$ and $y_{U^{4+}}^C$ are the lattice site-fraction of each cationic components and G^E is the excess molar Gibbs free energies. The latter can be expressed as:

$$G^E = \sum_i L_{U^{4+},M^{3+}:Cl^-}^i (y_{U^{4+}}^C - y_{M^{3+}}^C)^i y_{U^{4+}}^C y_{M^{3+}}^C \quad (7.3)$$

The composition triangle for the UCl_4 solid-solution model is shown in **Fig. 7.1** with three different corners. The hypothetical compound MCl_3 with the UCl_4 -type structural form located at the neutral line is obtained by 0.75 moles of $(\text{M}^{3+})_1(\text{Cl}^-)_4$ and 0.25 moles of $(\text{M}^{3+})_1(\text{Va}^0)_4$.

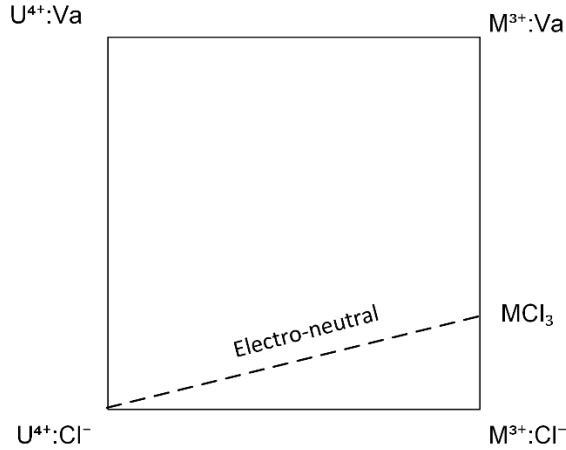
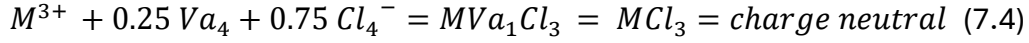


Fig. 7. 1: Geometric representation of thermodynamic models for the UCl_4 solid-solution phase ($M = \text{Ce, Pu}$).

The relationship between the Gibbs energies of hypothetical MCl_3 and the charged species $(\text{M}^{3+})_1(\text{Va}^0)_4$ and $(\text{M}^{3+})_1(\text{Cl}^-)_4$ can be defined as Eq. 7.5-7.8:

$${}^0G_{\text{M}^{3+}:\text{Cl}^-}^{\text{UCl}_4\text{ss}} = {}^0G_{\text{MCl}_3(s)} \quad (7.5)$$

$${}^0G_{\text{U}^{4+}:\text{Cl}^-}^{\text{UCl}_4\text{ss}} = {}^0G_{\text{UCl}_4(s)} \quad (7.6)$$

$${}^0G_{\text{U}^{4+}:\text{Va}^0}^{\text{UCl}_4\text{ss}} = {}^0G_{\text{UCl}_4(s)} - 2 {}^0G_{\text{Cl}_2(g)} \quad (7.7)$$

$${}^0G_{\text{M}^{3+}:\text{Va}^0}^{\text{UCl}_4\text{ss}} = {}^0G_{\text{MCl}_3(s)} - 1.5 {}^0G_{\text{Cl}_2(g)} \quad (7.8)$$

$${}^0G_{\text{M}^{3+}:\text{Cl}^-}^{\text{UCl}_4\text{ss}} = {}^0G_{\text{MCl}_3(s)} + a_1 + b_1 T \quad (7.9)$$

Where ${}^0G_{\text{UCl}_4(s)}$ is the Gibbs energy function of pure UCl_4 (s), ${}^0G_{\text{MCl}_3(s)}$ is the Gibbs energy function of pure MCl_3 (s) ($M = \text{Ce, Pu}$), ${}^0G_{\text{Cl}_2(s)}$ is the Gibbs energy function

of pure Cl_2 (g) and parameter a_1 and b_1 are adjustable parameters determined by the experimental solid-solubility found on the phase diagram.

The following a_1 and b_1 parameter were set for each binary system $\text{MCl}_3\text{-UCl}_4$:

$${}^0G_{\text{U}^{4+};\text{F}^-}^{\text{MF}_3\text{ss}} = 73000 - 147 \cdot (T/K) \quad (7.8)$$

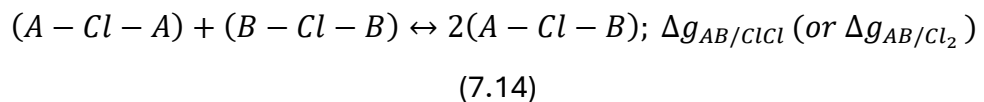
The finalised Bragg-Williams excess Gibbs energy parameters for the binary system $\text{MCl}_3\text{-UCl}_4$:

$${}^0L_{\text{M}^{3+},\text{U}^{4+};\text{Cl}^-,Va}^{(MU)\text{Cl}} = -24 \cdot (T/K) \quad (7.9)$$

7.4.3 Thermodynamic modelling for liquid solution

The quadruplet approximation in the quasi-chemical model (QCM), proposed by Pelton and Chartrand (2000) [60] was used to model the excess Gibbs energy of the liquid phase. The later model introduced the quadruplet approximation by Chartrand (2001) [28], which consists of two sub-lattices, one consisting of cations A and B and anion F^- (in this work only fluoride anion is present). The quadruplet is the fundamental unit in this updated model. In previous models, i.e. QCM pair approximation, either the first-nearest neighbour (FNN) interactions or the second-nearest neighbour (SNN) were modelled to be the dominant influence on the excess terms. The quadruplet approximation is updated and treats FNN and SNN interactions simultaneously for determining optimised excess parameters of the liquid solution.

The transfer reaction between FNN and SNN pairs is expressed as:



$\Delta g_{AB/\text{Cl}}$ is an empirical parameter and may be composition dependant, if $\Delta g_{AB/\text{Cl}_2} = 0$ then random mixing occurs, if $\Delta g_{AB/\text{Cl}_2} < 0$, then Eq. 7.14 is displaced to the right with (A-Cl-B) pairs becoming predominant.

The Gibbs energy change $\Delta g_{AB/\text{Cl}}$ associated with the SNN-FNN reaction is given by:

$$\Delta g_{AB/Cl_2} = \Delta g_{AB/Cl_2}^0 + \sum_{i \geq 1} g_{AB/Cl_2}^{i0} x_{AB/Cl_2}^i + \sum_{j \geq 1} g_{AB/Cl_2}^{j0} x_{AB/Cl_2}^j \quad (7.15)$$

Where $\Delta g_{AB/Cl_2}^0$ and g_{AB/Cl_2}^{i0} are composition independent coefficients that may vary with temperature. Note that the terms with subscript $_{AB/F_2}$ and $_{AB/F_2}$ represent the same pairs and can be used interchangeably. x_{AB/Cl_2}^i is composition dependant function, defined as the fraction to cation-cation pair mole fractions X_{AA} , X_{AB} and X_{BB} :

$$x_{AB/Cl_2} = \frac{X_{AB/Cl_2}}{X_{AA/Cl_2} + X_{AB/Cl_2} + X_{BB/Cl_2}} \quad (7.16)$$

As the composition of the binary systems changes, the quadruplet approximation model must maintain other parameters to satisfy the conservation of charge whilst simultaneously considering how the FNN and SNN coordination number varies. By assuming the cation SNN coordination number and the charges of cation/anion remain constant, the anion SNN coordination number is fixed in the quadruplet by:

$$\frac{q_A}{Z_{AB/Cl_2}^A} + \frac{q_B}{Z_{AB/Cl_2}^B} = \frac{q_{Cl}}{Z_{AB/Cl_2}^{Cl}} + \frac{q_{Cl}}{Z_{AB/Cl_2}^{Cl}} \quad (7.17)$$

Where q_i are the charges of anions and cations, and Z_{AB/Cl_2}^i are the SNN coordination number of the respective ion in each quadruplet. For each both end members, the quadruplet formations include (A-Cl-A), (A-Cl-B), (B-Cl-B) SNNs. Their excess Gibbs energy expressions are expressed $\Delta g_{AA/Cl_2}$, $\Delta g_{AB/Cl_2}$ and $\Delta g_{BB/Cl_2}$.

The current work re-introduces M_{vi}^{3+} (with coordination number in indices) into the pure liquid MF₃ as the same complex and surrogate complexes were identified in Raman spectroscopy studies with MF₃ and AF mixtures (A = Li, Na, K; M = Ce, Pu) from the previously optimised RbCl-CeCl₃ and RbCl-PuCl₃ models by Findlay et al. (2025) [33]. This permits one composition of second nearest neighbour-short range ordering (SNN-SRO). There was no evidence for formation of M_{iv}^{3+} four-coordinated M³⁺ within melts, but there was for the six-coordinated complex, corresponding to the [MCl₆]³⁻ “complex-anion”.

The current work re-introduces a mixture of U_v^{4+} , U_{vi}^{4+} and U_{vii}^{4+} into the pure liquid UCl₄, consistent with the same complexes and surrogate complexes identified in recent Raman spectroscopy studies discussed in Chapter 3. This permits three different compositions of second nearest neighbour-short range ordering (SNN-SRO). U_v^{4+} is the five-coordinated U⁴⁺, corresponding to the [UCl₅]⁻ “complex-anion”, U_{vi}^{4+} is the six-coordinated U⁴⁺, corresponding to the [UCl₆]²⁻ “complex-anion” and U_{vii}^{4+} is the seven-coordinated U⁴⁺, corresponding to the [UCl₇]³⁻ “complex-anion”.

For the model to maintain mass balance and for conservation of charge, the three different uranium complexes balance with the according Rb⁺ cations as SNNs. Following this methodology, the following complexes [UCl₅]⁻, [UCl₆]²⁻ and [UCl₇]³⁻ have SRO at compositions at X(UCl₄) at 0.5, 0.333 and 0.25 respectively. The results show that this model excluding any dimers can satisfactorily reproduces all experimental phase diagram data and predicted enthalpy of mixing.

Building on the Raman spectroscopy analysis and thermodynamic modelling discussed in Chapter 3, the g^0 values in Equations 7.19–7.24 were selected to allow the six-coordinated complex [UCl₆]²⁻ to dominate in the melt. This aligns with experimental findings from Photiadis et al. (1999) [96], which confirmed [ThCl₆]²⁻ as the primary species, with [ThCl₇]³⁻ also present in smaller quantities, particularly on the ThCl-rich side. Early modelling attempts included only these two complexes but were unable to reproduce the phase diagram while preserving the enthalpy of mixing and the composition of maximum short-range order at X(UCl₄) = 0.35. Further refinement, informed by analogous studies on AlkCl–HfCl₄ (Alk = Li, Na, K, Rb) systems by Smirnov et al. (1984) [105], led to the introduction of the [UCl₅]⁻ complex. Including this species successfully reproduced the phase diagram while maintaining the calculated enthalpy of mixing and compositional minima.

The resulting molten salt binary system has the Gibbs free energy calculation by the Factsage software by summing the Gibbs free energies of the various quadruplets along with the energy contributed by the configurational entropy resulting from the distribution of the quadruplets on the lattice sites as expressed below:

$$G = \sum_{i=A} \sum_{j=B} \sum_{k=F} n_{ij/kk} g_{ij/k}^0 - T\Delta S^{config} \quad (7.18)$$

Where $n_{ij/kk}$ is the number of moles of the ij/kk quadruplet, $g_{ij/k}^0$ is the molar Gibbs free energy of the ij/k quadruplet, and ΔS^{config} is the configurational entropy of mixing. A definitive mathematical description of the entropy term is not presently established; however, an appropriate expression was proposed by Pelton et al. [60]. The approximation was later improved by Chartrand et al. [28] that was able to treat FNN and more recently SNN SRO. $n_{ij/kk}$ is the internal variable which requires a minimisation of the Gibbs free energy of the molten salt binary solution at a known temperature, pressure and composition – this embodies the equilibrium configuration of both the FNN and SNN. Although the SNN numbers are not used to physically characterise the complexes within the salt solution, they are model parameters which allows to define the composition of which maximum SRO occurs for each complex. This is constrained by charge neutrality, by **Eq. 7.10** and following Z numbers used in this model in **Table 7.3**.

Table 7. 3: SNN “coordination numbers” for quadruplets ABXX used in the MQMQA for the liquid.

A	B	X	$Z_{AB/XX}^A$	$Z_{AB/XX}^B$	$Z_{AB/XX}^X$	$Z_{AB/XX}^X$
Rb	Ce _{vi}	Cl	2.4	7.2	2.4	2.4
Rb	Pu _{vi}	Cl	2.4	7.2	2.4	2.4
Rb	U _v	Cl	6	6	2.4	2.4
Rb	U _{vi}	Cl	3.6	7.2	2.4	2.4
Rb	U _{vii}	Cl	8.4	2.8	2.4	2.4
U _v	U _{vi}	Cl	6	7.2	1.36364	1.36364
U _v	U _{vii}	Cl	6	8.4	1.75	1.75
U _{vi}	U _{vii}	Cl	7.2	8.4	1.93846	1.93846
U _{v-vii}	Ce _{vi}	Cl	3	6	1.09091	1.09091
U _{v-vii}	Pu _{vi}	Cl	3	6	1.09091	1.09091

Lastly, the $\Delta g_{AB/Cl_2}$ of all the quadruplets were manually optimised without the use of Optisage software to fit the previous and new experimental phase diagram data explored in this work – alongside the anticipated enthalpy of mixing. The Gibbs energy function $\Delta g_{AB/F_2}$ within the Factsage software is given by equation: such as:

$$\Delta g_{AB/Cl_2} = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E \cdot T^3 \quad (7.19)$$

Where coefficients, A-E, are optimised individually to achieve the best possible fit to the data.

In future studies involving different salt mixtures, the same cation may form alternative coordination environments beyond the six-coordinated complex. To ensure thermodynamic consistency, it will be necessary to apply minor corrections, introduced through manual iteration uniformly to the standard Gibbs energy expressions of all fluoride complexes. Careful documentation of these corrections will be essential to accurately assign each coordination species within varying chemical systems for future higher order systems containing this sub-system.

$$\Delta g_{RbCe_{iv}/Cl_2} = -16700 - 0.35 \cdot (T/K) - 4300 \cdot \chi_{RbCe_{iv}/Cl_2} - 1000 \cdot \chi_{Ce_{iv}Rb/Cl_2} + 4.2 \cdot (T/K) \chi_{Ce_{iv}Rb/Cl_2}^2 \quad (7.20)$$

$$\Delta g_{RbCe_{vi}/Cl_2} = -30100 - 2.3 \cdot (T/K) \cdot \chi_{Ce_{vi}Rb/Cl_2} - 3.7 \cdot (T/K) \cdot \chi_{RbCe_{vi}/Cl_2} + 2500 \cdot \chi_{RbCe_{vi}/Cl_2}^2 \quad (7.21)$$

$$\Delta g_{RbPu_{iv}/Cl_2} = -16900 - 6100 \cdot \chi_{Pu_{iv}Rb/Cl_2} - 2000 \cdot \chi_{RbPu_{iv}/Cl_2} + 10.0 \cdot (T/K) \cdot \chi_{Pu_{iv}/Cl_2}^2 - 6.0 \cdot (T/K) \cdot \chi_{Pu_{iv}Rb/Cl_2}^3 \quad (7.22)$$

$$\Delta g_{RbPu_{vi}/Cl_2} = -32000 - 3000 \cdot \chi_{RbCe_{vi}/Cl_2} + 4700 \cdot \chi_{RbPu_{vi}/Cl_2} + 2.1 \cdot (T/K) \cdot \chi_{Pu_{vi}/Cl_2}^2 \quad (7.22)$$

$$\Delta g_{RbU_{vi}/F_2} = -51000 + 15425.9 \chi_{RbU_{vi}/F_2} - 1.1E^{-5} (T^3/K) \chi_{RbU_{vi}/F_2} \quad (7.22)$$

$$\Delta g_{RbU_{vii}/Cl_2} = -26000 - 19.5 \cdot (T/K) \quad (7.23)$$

$$\Delta g_{RbU_{vi}/Cl_2} = -35000 - 1.2 \cdot (T/K) + (2.7 \cdot T (T/K) \cdot \ln\left(\frac{T}{K}\right) \chi_{RbU_{vi}/Cl_2}) + (1.5 \cdot T (T/K) \cdot \ln(T/K) \chi_{U_{vi}Rb/Cl_2}) \quad (7.24)$$

$$\Delta g_{RbU_v/Cl_2} = -37000 + 2.8 \cdot T (T/K) \cdot \ln (T/K) + (-10000 + 2.7 \cdot T (T/K) \cdot \ln (T/K)) \cdot \chi_{U_vRb/Cl_2} \quad (7.25)$$

$$\Delta g_{Ce_{iv-vi}U_{v-vii}/Cl_2} = -4800 - 7000\chi_{U_{v-vii}Ce_{iv-vi}/Cl_2} - 7000\chi^2_{U_{v-vii}Ce_{iv-vi}/Cl_2} \quad (7.26)$$

$$\Delta g_{Pu_{iv-vi}U_{v-vii}/Cl_2} = -4800 - 7000\chi_{U_{v-vii}Pu_{iv-vi}/Cl_2} - 7000\chi^2_{U_{v-vii}Pu_{iv-vi}/Cl_2} \quad (7.27)$$

7.5 Experimental method

High-purity CeCl₃ and UCl₄ anhydrous powders were prepared and handled under inert argon in a glovebox. Custom Ni-201 crucibles with SUS316L lids, specifically designed for fluoride salt studies, were used to ensure hermetic sealing, high thermal conductivity, and compatibility at elevated temperatures. All crucibles were rigorously cleaned and dried prior to use. Thermal analyses were performed with a Hitachi STA-7200 TGA-DSC under flowing argon, with calibration against standard salts and metals to ensure accuracy in enthalpy and temperature determination. Hermetically sealed salt mixtures were loaded in the STA-7200 furnace and subjected to controlled heating-cooling cycles, with TGA used to track volatilisation and DSC to determine melting and solid-solid transitions. This methodology, established in previous chapters by Findlay et al. [33], [35],[34] provides a reproducible and sensitive framework for studying the thermodynamics of CeCl₃-UCl₄ mixtures, and serves as the foundation for future extension to other actinide-lanthanide fluoride systems.

7.6 Results & Discussion

7.6.1 The $\text{CeCl}_3\text{-UCl}_4$ system

There are relatively few DSC or thermal analysis studies on $\text{MCl}_3\text{-UCl}_4$ binary systems, where $\text{M} = \text{Ce, U, Pu}$ and $\text{Ac} = \text{Th, U}$. Early phase diagram data for $\text{UCl}_3\text{-UCl}_4$ were reported by Kraus (1943) [166] and reported immiscibility – contradicting the results from Desyatnik et al. (1970) [167]. Building on this, Vorobei (1971) [168] experimentally investigated the $\text{ThCl}_4\text{-PuCl}_3$ system, which was later thermodynamically optimized by Dumaire (2022) [169]. Their work demonstrated the solubility of PuCl_3 in ThCl_4 , as opposed to the solubility of UCl_4 in UCl_3 considered in the present study. However, because U^{3+} exhibits a larger ionic radius difference relative to U^{4+} than Pu^{3+} does to Th^{4+} , it was more appropriate in this work to model an anticipated solid solution behaviour on the UCl_4 -rich side of the system.

For the first time, the $\text{CeCl}_3\text{-UCl}_4$ system has been explored with DSC in this work and remodelled to account for vacancies on the anion side with the UCl_4 solid lattice structure that chloride vacancies are creating with increase CeCl_3 content. Interestingly, there was no clear DSC event that occurred during heat, but one did occur during all three cooling cycles at 769 K, therefore, this data was taken as the eutectic temperature shown in **Fig. 7.3**:

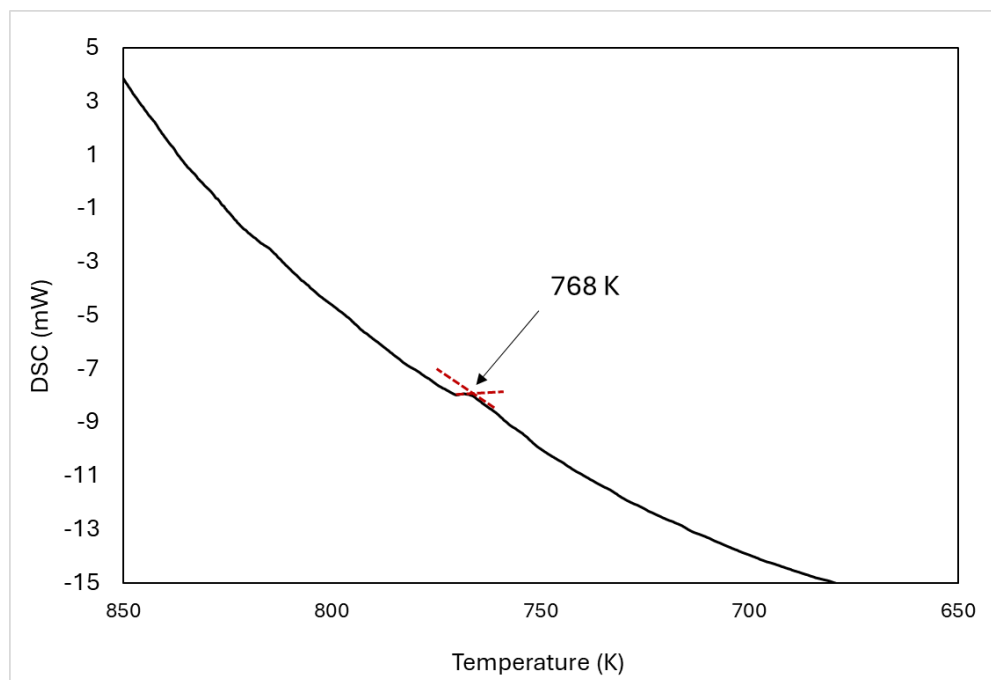


Fig. 7. 2: DSC cooling cycle at 5 K min^{-1} composition $0.333 \text{ mol UCl}_4 - 0.667 \text{ mol CeCl}_3$.

In modelling the $\text{CeCl}_3\text{-UCl}_4$ and $\text{PuCl}_3\text{-UCl}_4$ binary solid solutions, vacancies were explicitly incorporated on the rare-earth fluoride sublattice rather than assuming a simple substitutional exchange between U^{3+} and U^{4+} cations. It remains uncertain whether simple interstitial cation substitution occurs within this salt system. While such a mechanism would be easier to model for maintaining charge balance at a fixed ratio, it is more likely that vacancies play a dominant role in achieving charge compensation. Incorporating vacancies within the compound energy formalism allows the models to account for both the configurational entropy arising from defect populations and the enthalpic effects of vacancy–cation interactions. This approach provides a thermodynamically consistent representation of the experimentally observed non-stoichiometry and enhances predictive accuracy for key physical properties such as ionic diffusion, conductivity, density, and thermal transport. Establishing this framework is therefore critical for extending CALPHAD-based descriptions to more complex actinide chloride systems, where accurate defect modelling will be central to understanding fuel salt chemistry and

performance. Future experimental DSC measurements could be used to further validate this model for better reliability.

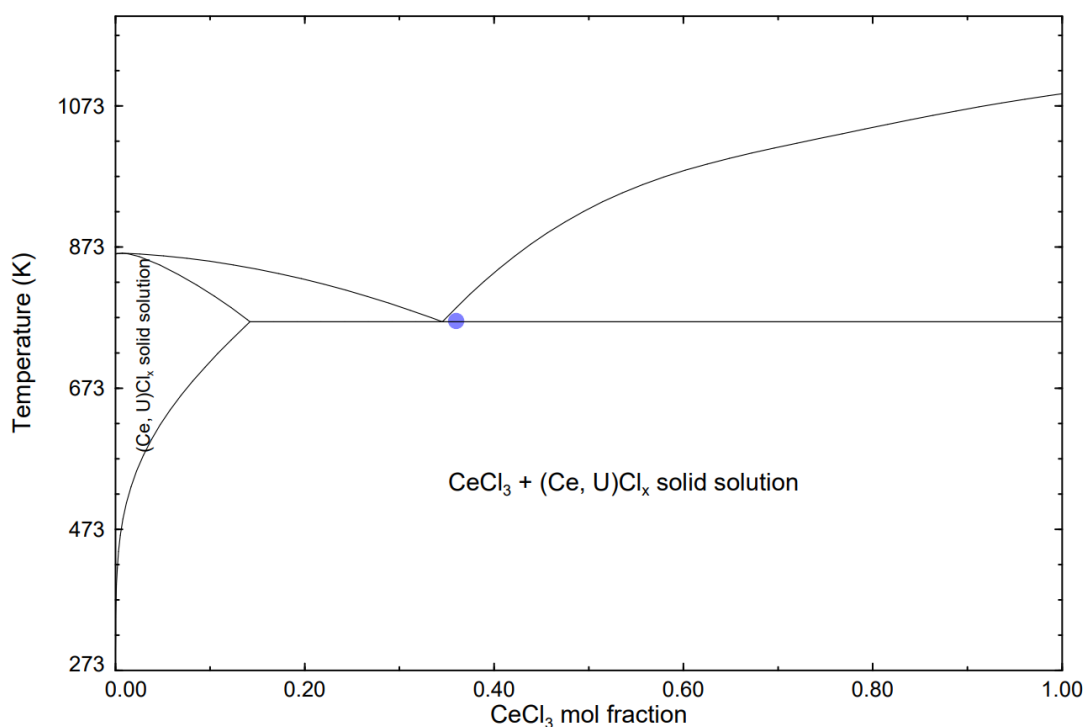


Fig. 7. 3: Optimised $\text{CeCl}_3\text{-UCl}_4$ phase diagram, ● J. Findlay DSC cooling, 5 K min^{-1} (this work).

7.6.2 The $\text{PuCl}_3\text{-UCl}_4$ system

The $\text{PuCl}_3\text{-UCl}_4$ system was modelled using the same thermodynamic framework established for the $\text{CeCl}_3\text{-UCl}_4$ system, incorporating all relevant experimental and assessed data from previous studies. This consistent approach ensures compatibility across the chloride phase diagram assessments and allows reliable extrapolation of mixing behaviours and phase equilibria within the actinide trichloride–tetrachloride systems.

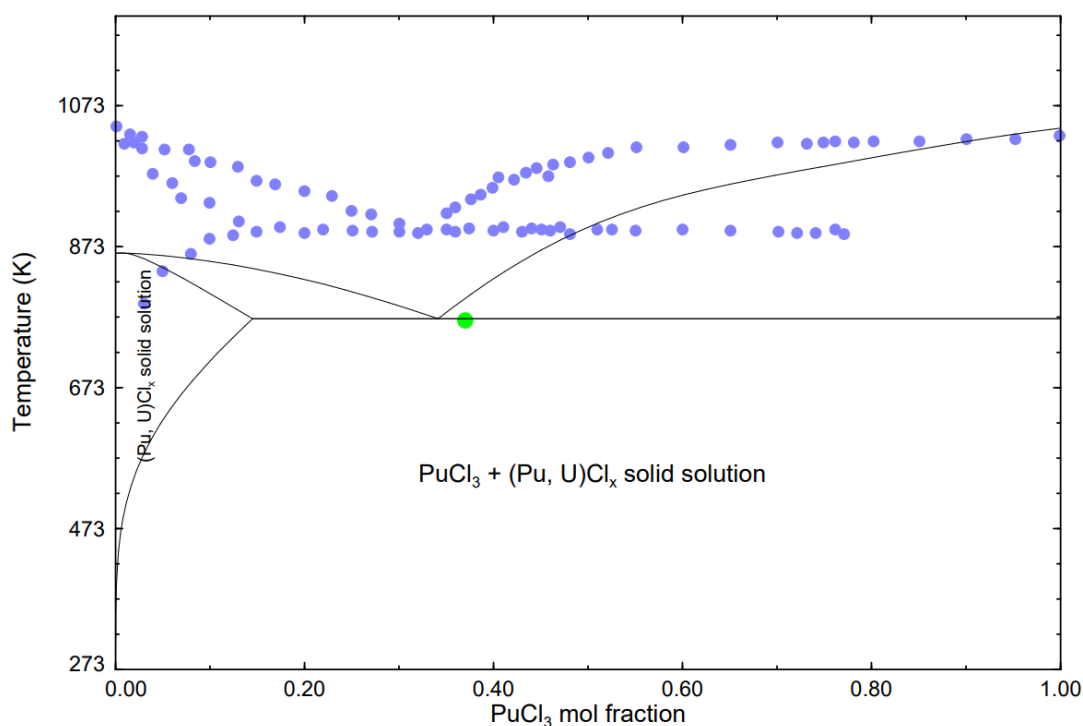


Fig. 7. 4: Optimised $\text{PuCl}_3\text{-UCl}_4$ phase diagram, ● $\text{PuCl}_3\text{-ThCl}_4$ Vorobei et al. (1971) [168], ● $\text{CeCl}_3\text{-UCl}_4$ J. Findlay DSC cooling, 5 K min^{-1} (this work).

Future experimental work is necessary to validate this thermodynamic model for increased reliability.

7.6.3 The $\text{RbCl-CeCl}_3\text{-UCl}_4$ system

Optimising the reciprocal sub-binary systems with the $\text{RbCl-CeCl}_3\text{-UF}_4$ ternary phase diagram using the manual iterative technique combined with determining the various ionic complexes within the molten salts aids in preserving reliability of the model. It is well established that specific molten salts mixtures, do not exhibit a random mixing of cation and anion species, rather they form clusters at specific concentrations, largely in part to each of the species ionic radii/charge ratio. This phenomenon is far more pronounced in MSR fuels where certain alkali metal fluorides are combined with lanthanide and actinide fluoride salts. Known as SRO (short range ordering), the likes Factsage software is built upon, first conceptualised by Pelton, and further developed by Patrice Chartrand in the MQMQA (modified quasi-chemical model in the quadruplet approximation) [28].

Chapter 7: Thermodynamic investigation of the CeCl₃-UCl₄ system and the RbCl-MCl₃-UCl₄ systems (M = Ce, Pu)

The most beneficial aspect of carrying out the Gibbs energy optimisations manually and assigning Gibbs energy functions to each of the complexes within the melts for each binary sub-system, rather than the quicker more common method of assigning the Gibbs energy function to the composition/concentration of a singular end-member component, i.e. [UCl₅]⁻, [UCl₆]²⁻ and [UCl₇]³⁻ instead of pure UCl₄, is that when the higher order systems, ternary and quaternary, complexity increase but the model maintains reliability. This is also highlighted by previous work in the literature for ternary systems where excess ternary Gibbs energy parameters need to be introduced into the model. These are based on geometric weightings of the mole fractions of each pure end-member component. Such mathematical formula based on the geometric weightings as split into the Kohler, Kohler/Toop, Muggianu and the Muggianu/Toop approximations. The variety are based upon whether the ternary system phase diagram is either asymmetric or symmetric in nature. The ternary phase diagram with all four-phase intersection points with the molten salt solutions are given in **Table 7.4** and **Fig. 7.5**.

Table 7. 4: Four-phase equilibria intersection points in the RbCl-CeCl₃-UCl₄ system.

No.	X (UCl ₄)	X (RbCl)	X (CeCl ₃)	T (K)	Equilibrium	Solid phases in equilibria
1	0.26489	0.65421	0.08090	768.78	Peritectic	Rb ₂ CeCl ₅ , Rb ₃ CeCl ₆ (S2), Rb ₂ UCl ₆
2	0.21372	0.59244	0.19383	752.31	Eutectic	RbCe ₂ Cl ₇ (S2), Rb ₂ CeCl ₅ , Rb ₂ UCl ₆
3	0.27965	0.55584	0.16451	748.76	Eutectic	RbCe ₂ Cl ₇ (S2), CeCl ₃ , Rb ₂ UCl ₆
4	0.21297	0.78354	0.00348	714.80	Eutectic	Rb ₃ CeCl ₆ (S2), RbCl, Rb ₂ UCl ₆
5	0.41349	0.44252	0.14399	682.01	Eutectic	CeCl ₃ , Rb ₂ UCl ₆ , RbUCl ₅
6	0.43698	0.40033	0.16269	681.92	Eutectic	CeCl ₃ , (Ce, U)Cl _x (s.s.), RbUCl ₅

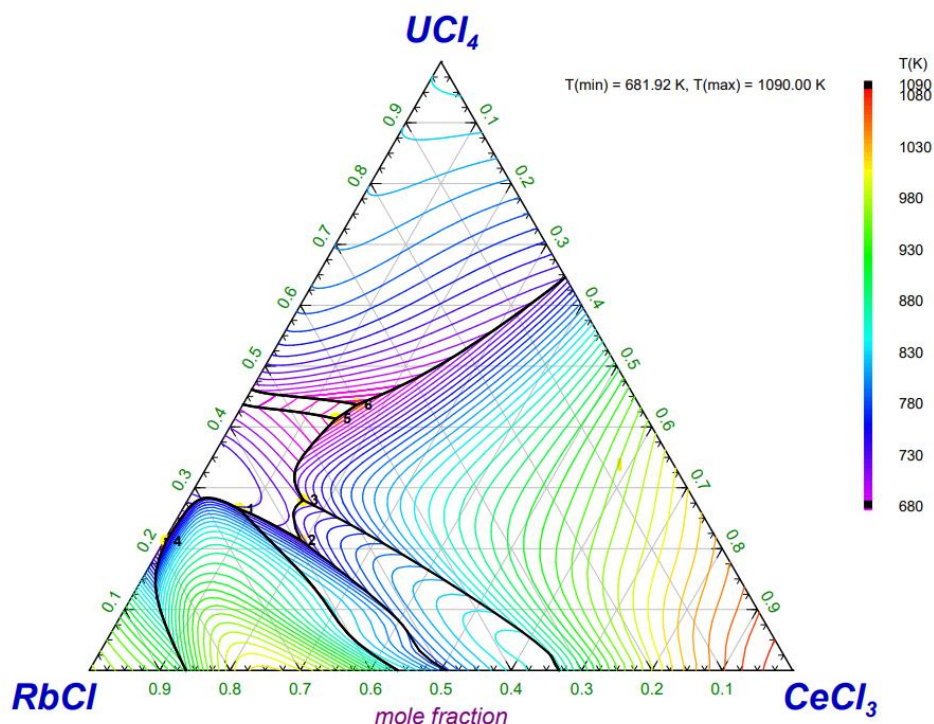


Fig. 7. 5: $\text{RbCl-CeCl}_3\text{-UCl}_4$ ternary phase diagram, four-phase intersection points 1-15 details provided in **Table 7.4**.

7.6.4 The $\text{RbCl-PuCl}_3\text{-UCl}_4$ system

Integrating the sub binary systems RbCl-PuCl_3 and RbCl-UCl_4 from the previous chapters, and the newly optimised $\text{PuCl}_3\text{-UCl}_4$ system in this chapter enable the ternary system $\text{RbCl-PuCl}_3\text{-UCl}_4$ to be calculated in this work.

The ternary phase diagram with all four-phase intersection points with the molten salt solutions are given in **Table 7.5** and **Fig 7.6**.

Table 7. 5: Four-phase equilibria intersection points in the $\text{RbCl-PuCl}_3\text{-UCl}_4$ system.

No.	X (UCl_4)	X (RbCl)	X (PuCl_3)	T (K)	Equilibrium	Solid phases in equilibria
1	0.25102	0.67432	0.07466	764.42	Peritectic	Rb_2PuCl_5 , Rb_3PuCl_6 (S2), Rb_2UCl_6
2	0.26729	0.56096	0.17176	751.02	Eutectic	RbPu_2Cl_7 (S2), Rb_2PuCl_5 , Rb_2UCl_6
3	0.19201	0.58822	0.21978	746.54	Eutectic	RbPu_2Cl_7 (S2), CeCl_3 , Rb_2UCl_6
4	0.20084	0.78403	0.01513	713.16	Eutectic	Rb_3PuCl_6 (S2), RbCl , Rb_2UCl_6
5	0.43723	0.42151	0.14126	688.92	Eutectic	PuCl_3 , Rb_2UCl_6 , RbUCl_5
6	0.41675	0.45727	0.12598	688.42	Eutectic	PuCl_3 , $(\text{Ce, U})\text{Cl}_x$ (s.s.), RbUCl_5

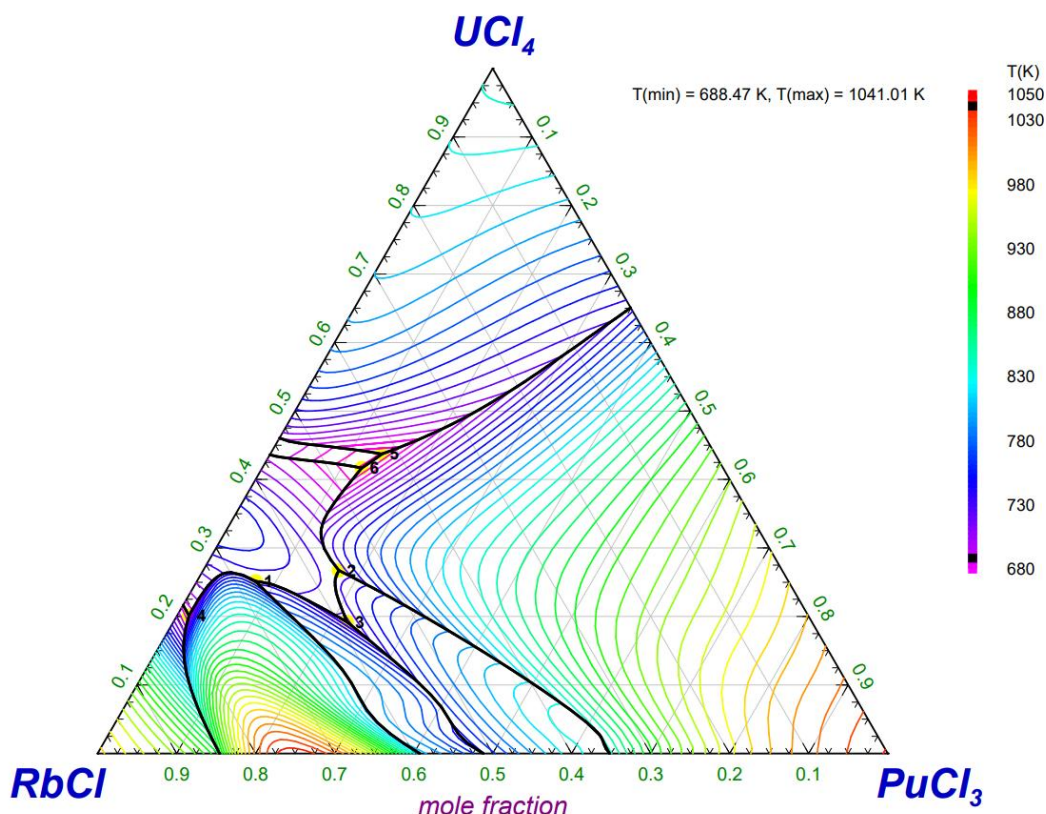


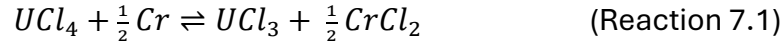
Fig. 7. 6: RbCl - PuCl_3 - UCl_4 ternary phase diagram, four-phase intersection points 1-15 details provided in **Table 7.5**.

7.6.5 Redox control, corrosion mitigation and tellurium embrittlement

As outlined in previous chapters, corrosion in molten salt reactors (MSRs) is fundamentally governed by Gibbs free energy gradients arising from thermally induced differences in chemical potential [75]. In the Molten Salt Reactor Experiment (MSRE), researchers at Oak Ridge National Laboratory (ORNL) demonstrated that careful control of the redox potential was essential for mitigating alloy corrosion, leading to the adoption of high-nickel alloys such as Hastelloy-N in place of chromium-bearing stainless steels [78].

This approach relied on shifting the $\text{U}^{4+}/\text{U}^{3+}$ ratio in the LiF - BeF_2 - ZrF_4 - UF_4 fuel salt toward more reducing conditions by increasing the U^{3+} content through a higher UF_3/UF_4 ratio, thereby suppressing chromium leaching. The effect arises from the oxidizing nature of UF_4 , as shown in Reaction 7.1. While such behaviour has been

extensively studied in fluoride systems, chloride-based salts have not been investigated to the same extent, though the underlying thermodynamics and chemical principles are expected to be similar.



Previous researchers [23] also noted that with too high UF₃/UF₄ ratio can make the fuel salt overly reducing, which was experimentally observed in the MSRE as increased uranium carbide formation on the surfaces of the graphite moderator, as shown by reactions (2–3). This occurred because UCl₃ has a significantly lower redox potential (as illustrated in Fig. 20). However, in the MSFR, no moderator or graphite is present, so these carbide-forming reactions cannot occur under the same conditions.



Heavier and larger alkali cations such as Rb⁺, present in RbCl, promote stronger complex formation with UCl₄, producing a more negative Gibbs free energy in the liquid binary system. Consequently, the activity of UCl₄ within the melt decreases (also calculated and highlighted in chapter 3), while the activity of the [UCl_x]ⁿ⁻ and [PuCl_x]ⁿ⁻ complexes increases due to their greater thermodynamic stability. Although the proposed hypothesis is preliminary and open to evaluation, it is further supported by the results from this thermodynamic assessment carried out in this chapter, shown in **Fig. 7.7**, where the addition of RbCl and PuCl₃ significantly lowers the Gibbs energy and thus lowering the redox potential compared to FLiBe-based UF₄ fuel salt, making chromium leaching far less thermodynamically favourable. A particularly interesting aspect is that this reintroduces the possibility of reducing the redox potential of the fuel salt without the addition of UF₃, while still maintaining conditions that are also thermodynamically unfavourable for uranium carbide formation via the pathways illustrated in reactions 7.2 and 7.3.

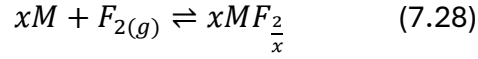


Similarly, PuCl_3 , with similar properties to UCl_3 would be expected to form analogous comparable carbides as described in Reactions 7.4 & 7.5. Using thermodynamic data from Gurvich [68], interestingly, the Gibbs energy change of plutonium carbides formation is positive across all MSR-relevant temperatures. Additionally, CeCl_3 has been experimentally shown to form stable and $[\text{MCl}_4]^-$ and $[\text{MF}_6]^{3-}$ complexes in RbCl solutions, and PuCl_3 is expected to exhibit analogous complexation behaviour due to its close chemical similarity, resulting in similarly more negative Gibbs energies within the binary systems. This mechanism would, in theory, further suppress the thermodynamic propensity for plutonium carbide formation at the graphite moderator interface.

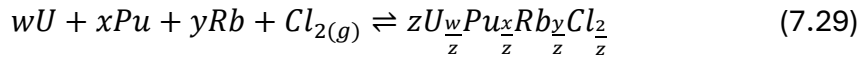
It not properly understood the exact mechanisms of the variations in the oxidation state between the $\text{U}^{3+} / \text{U}^{4+}$ within a molten $\text{UCl}_3/\text{UCl}_4$ chloride salt solution, and it may be possible that the change in oxidation state of $\text{Pu}^{3+} / \text{U}^{4+}$ conversion with a $\text{PuCl}_3/\text{UCl}_4$ solution, due to chemical differences between Pu and U rather than U being the same element. Enriched LiF and BeF_2 may have superior neutronics in the thermal spectrum, having very low neutron absorption cross-section – which is most important for a high performance $^{232}\text{Th}/^{233}\text{U}$ thermal breeder MSR where excess neutrons from thermal based fission are low. However, the neutronic properties in a fast reactor are very different.

The enthalpy of mixing – although not the only thermodynamic parameter – is significant and contributes largely to the total Gibbs energy of a molten salt solution. Using heavier and larger cationic KCl and RbCl salts in binary systems with ZrCl_4 , ThCl_4 , UFCl_4 have far more negative total Gibbs energies than with lighter carrier salts such as LiCl and BeCl_2 . The thermodynamic properties were applied in the *FactSage 8.3*.

An Ellingham diagram is used here to illustrate the Gibbs free energy changes of reactions between alloying components and various salts as a function of temperature. The Gibbs free energy change of these formation reactions per mol of Cl_2 (g) can be simplified as:



Where x is the stoichiometric coefficient to balance the reaction per mole of pure Cl₂ gas, M is metal element (M = Mo, Ni, Fe, Cr, Mn, U, Pu, Rb) of the fuel or alloy component. Or in the case of the formation of the ternary molten salt solution in this work:



Where y and z are additional stoichiometric coefficients to balance the reaction per mole of pure Cl₂ gas for the RbCl-PuCl₃-UCl₄ solution.

The Gibbs free energy of the forward reaction per mole of Cl₂(g) in Equation 7.25 can then be written as:

$$\Delta G_r^\circ = xG_{MCl_{\frac{2}{x}}}^\circ - \left(xG_M^\circ + xG_{Cl_{2(g)}}^\circ \right) \quad (7.30)$$

Similarly for equation 26, the Gibbs free energy of the forward reaction per mole of Cl₂(g) for the RbF-PuF₃ solution:

$$\Delta G_r^\circ = zG_{U_{\frac{w}{z}}Pu_{\frac{x}{z}}Rb_{\frac{y}{z}}Cl_{\frac{2}{z}}}^\circ - \left(wG_U^\circ + xG_{Pu}^\circ + yG_{Rb}^\circ + xG_{Cl_{2(g)}}^\circ \right) \quad (7.31)$$

Here, in this work, the newly modelled RbCl-PuCl₃-UCl₄ system, two ternary eutectics redox potentials are plotted against other pure salts components including alloy corrosion products in **Fig. 7.7**:

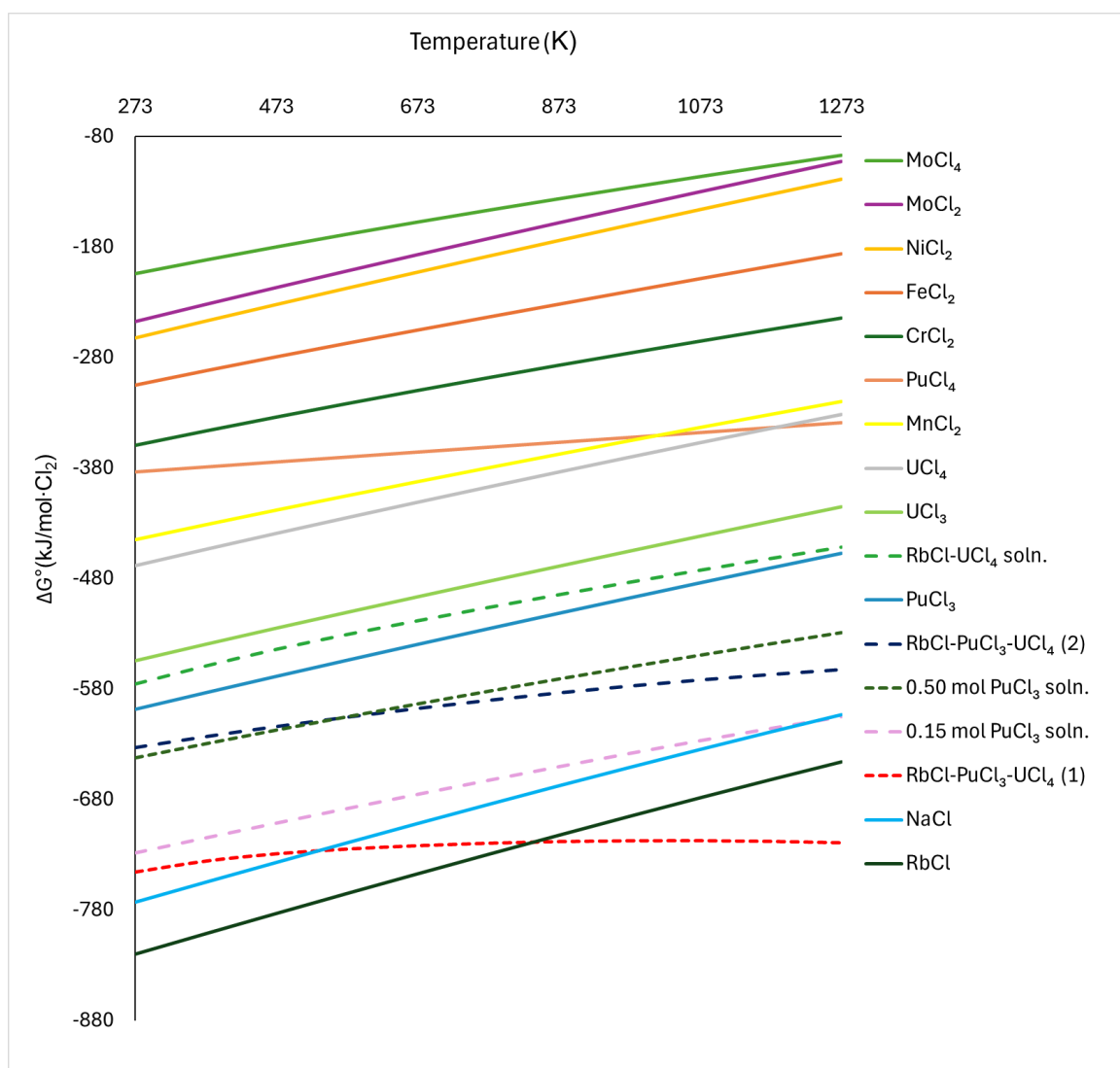


Fig. 7. 7: Standard Gibbs free energy of formation per mole of Cl_2 for salt components, corrosion products and molten salt solution ternary eutectic; $\text{RbCl-PuCl}_3\text{-UCl}_4$ (1) = 32.496 mol% RbCl – 10.890 mol% PuCl_3 – 33.708 mol% UCl_4 and second eutectic; $\text{RbCl-PuCl}_3\text{-UCl}_4$ (2) = 58.367 mol% RbCl – 21.808 mol% PuCl_3 – 19.052 mol% UCl_4 modelled in this work. Other data from Gurvich [68].

Tellurium-induced cracking remains a notable concern when considering chloride-based molten salt systems. Although the chemistry and thermodynamic processes of tellurium are expected to follow similar mechanisms as those observed in fluoride systems, the substitution of chloride for fluoride introduces subtle differences in thermodynamic behaviour. As in the MSRE, Te can exist in multiple oxidation states (e.g., Te^{-2} , Te^{-1} , Te^0 , Te^{+2} , Te^{+4} , Te^{+6}), and its interaction with the primary alloying elements in structural materials is critical. Based on insights from fluoride salts, Te species are not expected to react uniformly across alloy surfaces but will

likely accumulate at Te-rich regions along grain boundaries, forming intermediate Ni_xTe_y compounds that can lead to intergranular embrittlement.

Previous studies) [77] in fluoride salts showed that controlling the redox state of the fuel salt was the most effective strategy for mitigating Te-induced embrittlement. By analogy, in chloride systems, adjusting the proportion of reduced uranium species (e.g., $\text{UCl}_3/\text{UCl}_4$ ratio) is anticipated to similarly influence Te speciation and reactivity, though the thermodynamic equilibria will differ slightly due to the distinct anionic environment. Alloy modifications that proved beneficial in fluoride salts, such as titanium or niobium additions, are expected to provide comparable mitigation in chloride systems, albeit with differences in diffusion kinetics and corrosion behavior owing to the chloride medium. Overall, while the chloride salts will follow analogous chemical mechanisms, careful attention must be paid to the altered thermodynamics and kinetics introduced by the anion swap.

Importantly, prior experiments in fluoride systems were conducted in $\text{LiF-BeF}_2\text{-ThF}_4$ salts, which are only moderately reducing due to their relatively less negative Gibbs free energy and higher redox potential. Even within this environment, tellurium-induced cracking could be completely suppressed when the UF_4/UF_3 ratio was reduced below 7 ($\text{UF}_3 \approx 14.3 \text{ mol\%}$) during prolonged exposures at 973 K, demonstrating that sufficiently reducing conditions are critical for mitigating embrittlement. In chloride systems, the chemistry is expected to follow similar mechanistic trends, with Te accumulation along grain boundaries and intermediate alloy compounds forming, but the thermodynamics will differ slightly due to the anion swap.

For the $\text{RbCl-PuCl}_3\text{-UCl}_4$ system proposed for a molten salt fast reactor (MSFR), the absence of a graphite moderator removes the risk of uranium carbide formation. This allows the salt to operate under even more strongly reducing conditions without compromising the reactor, making it ideal for simultaneously suppressing chromium leaching and tellurium cracking. The strongly reducing environment $\text{RbCl-PuCl}_3\text{-UCl}_4$ is evidenced by the two identified ternary eutectics in **Fig. 7.10**: $\text{RbCl-PuCl}_3\text{-UCl}_4$ (1) = 32.50 mol% RbCl – 10.89 mol% PuCl_3 – 33.71 mol% UCl_4 , and

$\text{RbCl-PuCl}_3\text{-UCl}_4$ (2) = 58.37 mol% RbCl – 21.81 mol% PuCl_3 – 19.05 mol% UCl_4 . Both compositions demonstrate very high solubility for PuCl_3 and UCl_4 , confirming that these mixtures can achieve highly reducing conditions while maintaining very high actinide solubility – ideal for a MSFR with high neutron flux at fast spectrum.

Analogous to fluoride studies, careful control of redox conditions in these chloride salts is expected to strongly influence tellurium speciation, chromium corrosion, and overall alloy compatibility. Unlike LiF-BeF_2 salts, the RbCl -based system can exploit heavier, larger cation chemistry to enhance melt stability, increase actinide solubility, and maintain low redox potential without relying on additives such as UF_3 , which in fluoride systems risk creating overly reducing conditions. As a result, this system provides an ideal platform to explore high-Pu and high-U chloride fuels for fast reactor applications, while retaining the ability to finely tune thermodynamic properties for optimal material and chemical stability.

7.7 Conclusion

The $\text{RbCl-PuCl}_3\text{-UCl}_4$ system is a key ternary for assessing RbCl -containing plutonium- and uranium-based salts in molten salt fast reactors (MSFRs), as a proportion of ^{238}U within the UCl_4 fuel component will inevitably undergo neutron capture to ^{239}Pu under irradiation – but also ^{238}U and other higher long-lived fertile actinides such as ^{240}Pu , ^{237}Np and ^{241}Am will undergo fast-fission within the core. In this work, the system is experimentally investigated using CeCl_3 as a surrogate and thermodynamically modelled. The modelling accounts for $[\text{UCl}_7]^{3-}$, $[\text{UCl}_6]^{2-}$, $[\text{UCl}_5]^-$, $[\text{PuCl}_4]^-$ and $[\text{PuCl}_6]^{3-}$ complexes in the melt. Each of these species exhibits distinct short-range ordering behaviours at specific compositions, representing a novel advancement in the thermodynamic characterisation of MSR chloride fuel salts using FactSage software.

Including multiple complexes within the sub-binary systems improves the robustness of modelling higher-order systems. By contrast, conventional FactSage approaches assign Gibbs energy functions to the liquid solution based on a single

end-member composition (e.g., UCl_4). While convenient for simple systems with a single eutectic and few intermediate compounds, this approach is limited because it models short-range ordering at only one composition, which becomes increasingly inadequate as system complexity grows. Spectroscopic studies show that short-range ordering arises from specific complex formation rather than a random distribution of ions, highlighting the importance of capturing these interactions. In realistic MSR applications, such complexity is unavoidable due to the accumulation of fission products and corrosion components during operation. This is supported by DSC heating analysis of the $\text{RbCl-CeCl}_3\text{-UCl}_4$ system, where the model predicted a ternary eutectic that was validated experimentally.

Other identified eutectics exhibit relatively high melting temperatures, which are less attractive for reactor operation, though they maintain largely negative Gibbs energies that could enhance corrosion resistance. Future quaternary studies incorporating NaCl and KCl could reduce melting temperatures while preserving desirable thermophysical and neutronic properties.

The composition $\text{RbCl-PuCl}_3\text{-UCl}_4$ (1) = 32.50 mol% RbCl – 10.89 mol% PuCl_3 – 33.71 mol% UCl_4 , and $\text{RbCl-PuCl}_3\text{-UCl}_4$ (2) = 58.37 mol% RbCl – 21.81 mol% PuCl_3 – 19.05 mol% UCl_4 permit higher fissile loading potentially enabling smaller, more compact MSR cores and reducing critical component sizes and capital costs.

Consequently, $\text{RbCl-PuCl}_3\text{-UCl}_4$ emerges as a promising candidate for advanced chloride-based fuel salts, while $\text{RbCl-CeCl}_3\text{-UCl}_4$ also remains relevant as a surrogate system for fission product behaviour. The $\text{UCl}_3/\text{UCl}_4$ ratio is frequently cited in the literature to control redox potential and mitigate corrosion, yet systematic evaluation of redox potentials across thermodynamically characterized actinide chloride solutions - alongside their ability to form stable complexes that limit dissolution of alloying components - remains limited. This study addresses that gap using FactSage software and Ellingham diagrams.

Finally, this work highlights the importance of robust methods for determining thermodynamic properties in data-scarce systems. Extending Gibbs energy functions to include multi-coordinated plutonium and cerium complexes in sub-

Chapter 7: Thermodynamic investigation of the $\text{CeCl}_3\text{-UCl}_4$ system and the $\text{RbCl-MCl}_3\text{-UCl}_4$ systems ($\text{M} = \text{Ce, Pu}$)

binary systems, while maintaining reliability for higher-order systems, is supported by high-sensitivity DSC with low-mass crucibles. This approach enables efficient modelling with minimal sample consumption and waste. As a study of a ternary chloride system, these findings provide a critical foundation for future investigations into ternary and higher-order actinide-containing salts, supporting advanced fuel cycles and next-generation MSR technologies.

Chapter 8: Conclusion

8.1 The objectives of this thesis

1. Provide thermodynamic assessments of previously unexplored molten salt mixtures.
2. Design and fabricate DSC crucibles compatible with molten salts, as no suitable commercial crucibles are currently available.
3. Develop thermodynamic models of the mixtures using Gibbs energy functions defined by complex species (as identified in prior Raman spectroscopy studies), rather than as functions of individual end-member components. This is to improve model reliability and enable future studies to correlate other thermophysical properties - such as density, viscosity, vapor pressure, and electrochemical parameters - with these complexes. Identify and evaluate potential alternative fuel salt systems for MSR and MSFRs, considering both binary and ternary combinations.
4. Validate and refine existing data through comparison with newly obtained results; for example, by improving the RbF-PuF₃ system using CeF₃ as a more appropriate surrogate than LaF₃ (as used in Benes' model) and subsequently recalculating ternary systems such as RbF-PuF₃-UF₄ using the updated data.
5. Utilise the completed thermodynamic assessments within the *FactSage* software to analyse redox potentials, thereby providing an indication of the relative corrosivity of the salt mixtures and offering insights into how strong complexing with Rb salts may mitigate key corrosion mechanisms, including chromium leaching, tellurium-induced cracking, and graphite carbide formation.

8.2 Summary of the results

This body of work provides a comprehensive thermodynamic investigation into six rubidium-based actinide salt systems: RbCl-CeCl₃, RbCl-PuCl₃, RbCl-UCl₄, RbF-CeF₃, RbF-PuF₃, RbF-UF₄, four uranium-based plutonium/cerium salt systems: CeCl₃-UCl₄, PuCl₃-UCl₄, CeF₃-UF₄, PuF₃-UF₄ and subsequently four ternary systems RbF-CeF₃-UF₄, RbF-PuF₃-UF₄, RbCl-CeCl₃-UCl₄ and RbCl-PuCl₃-UCl₄. Collectively, these studies establish a unified framework for describing complex short-range ordering phenomena and coordination chemistry in molten salts relevant to next-generation molten salt reactor (MSR) fuel cycles.

By incorporating multi-coordinated actinide complexes into Gibbs energy formulations, guided by spectroscopic evidence and validated through carefully optimised differential scanning calorimetry (DSC) measurements, this work moves beyond the limitations of classical end-member thermodynamic modelling. The approach developed here demonstrates that accounting for four-, five-, and six-coordinated species significantly enhances model reliability and provides a means to link thermodynamic stability with other thermophysical and electrochemical properties. This methodology enables future research to correlate complex speciation with key performance metrics such as density, viscosity, vapor pressure, and redox potential.

Each binary system examined offers distinct advantages. The chloride systems (RbCl-PuCl₃ and RbCl-UCl₄) reveal multiple low-temperature eutectics and heavier carrier salt benefits that contribute to neutron spectrum hardening, improved fissile material loading, and thus enhanced flexibility in MSFR core design. The fluoride systems (RbF-PuF₃ and RbF-UF₄) exhibit similarly favourable eutectic behaviour at moderate temperatures and enable higher actinide solubility than lighter alkali fluoride counterparts, while simultaneously improving redox stability and mitigating corrosion potential. Together, these results highlight rubidium halides as promising alternatives to conventional lithium- and sodium-based salts for advanced fuel formulations.

The RbCl-UCl₄ system showed much lower temperature eutectics than its fluoride counterpart – yet the UCl₄ is far more volatile and oxidising (purely from thermodynamics standpoint) – but similarly to all the systems studied in this work – adds to the hypothesis that in combination with heavier alkali-metal salts promote complexation – thus drastically lowering the activity of the UCl₄ – which aids in thermodynamic stability, lowering volatility and redox potential.

In addition to advancing the thermodynamic understanding of these systems, this research refines experimental methodologies for molten salt analysis. The development and successful application of small, corrosion-resistant, hermetically sealed DSC crucibles allow precise measurement of thermal events using minimal sample quantities, thereby reducing radiological risk, material use, and waste generation.

Ultimately, this thesis establishes a solid scientific foundation for future studies of ternary and higher-order rubidium-based actinide systems. The methodologies and thermodynamic data generated here provide critical tools for modelling phase equilibria, redox behaviour, and actinide complexation in molten environments. These findings directly support the ongoing development of safe, efficient, and sustainable fuel cycles for next-generation molten salt reactors, contributing to the broader effort toward low-carbon energy generation and improved nuclear fuel stewardship.

8.3 Outlooks and suggestions for future work

When considering neutron capture cross-sections, several salt systems can be readily excluded as potential carrier salts for actinide-containing fuels. In uranium- and plutonium-based fuel mixtures, particularly those intended for thermal-spectrum MSRs, neutron absorption by the carrier salt can be different due to the variation in capture cross-sections at higher neutron energies.

Among fluoride-based systems, FLiBe remains one of the more attractive options, as both lithium and beryllium exhibit exceptionally low neutron absorption cross-

sections - an essential characteristic for thorium-based breeder reactors. The LiF-UF₄ binary also offers a simple, low-temperature eutectic, making it highly suitable for reactor operation. In comparison, the RbF-UF₄ system examined in this work features three eutectics that enable higher UF₄ solubility, but these occur at higher melting temperatures, which may limit its practicality. However, our modelling of the ternary RbF-PuF₃-UF₄ system demonstrated that the inclusion of additional actinide fluorides can reduce the eutectic temperature, suggesting that other compatible systems - such as those incorporating, for example, KF or CaF₂ - may yield even lower melting points while maintaining high actinide loading. These systems, along with analogous chloride-based mixtures, remain experimentally unexplored and warrant detailed thermodynamic and experimental investigation. Future studies should also evaluate their key thermophysical and chemical properties, including volatility, density, fission product retention, and corrosion potential.

Future work should aim to experimentally determine the enthalpy of mixing for key binary systems to validate and further refine the thermodynamic models developed in this study. Although the calculated values presented here provide a strong starting point, direct calorimetric measurements would not only capture the minimum enthalpy values but also reveal the full shape of the mixing curve across different compositions. The curvature of these profiles offers valuable insight into the number and stability of complexes forming at various actinide salt concentrations. Moreover, positive enthalpies of mixing can indicate the presence of immiscibility gaps, which may hold practical significance for fuel reprocessing and separation strategies. Complementary Raman spectroscopy studies should also continue to validate the existence and coordination environment of such complexes. As the enthalpy of mixing contributes a major component to the overall Gibbs energy, accurately quantifying it is crucial for enhancing model reliability and deepening the understanding of the fundamental thermodynamic interactions governing molten salt behaviour.

In conclusion, because experimental investigation and validation of molten salt systems are inherently time-consuming and resource-intensive, the initial focus should remain on thermodynamic assessment to determine whether a liquid phase

Chapter 8: Conclusions

is stable and compatible under reactor conditions. It is likely that an ideal molten salt composition does not exist; instead, achieving an optimal balance among melting temperature, chemical stability, neutron economy, and corrosion resistance will be necessary for the first generation of operational MSR

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Appendix

DSC calibration for Hitachi DSC for UF₄ / UCl₄ containing experiments in the UTGARD laboratory

The Hitachi TGA/DSC 7200 instrument was temperature-calibrated using indium and silver as reference materials, following the procedure outlined in the Hitachi user manual. A first-order calibration curve was applied. The calibration was subsequently validated by testing additional known calibrants, including KClO₄, Ag₂SO₄, CsCl (solid–solid transition and melting), BaCO₃, and Ag, confirming accuracy across a broad temperature range.

Table S1: Calibration test and uncertainty values

Calibrant	Transition type	T _{lit} (K)	T _{meas.} (K)	% Δ T _{meas.} error	T lit. / T meas.	Ref.
In	Fusion	429.75	430.85	0.22300	0.997446907	[67]
KClO ₄	Solid-phase transition	573.95	573.65	0.00000	1.000522967	[67]
Ag ₂ SO ₄	Solid-phase transition	699.35	698.75	-0.50702	1.000858676	[67]
CsCl	Solid-phase transition	749.15	749.35	-0.05255	0.999733102	[67]
CsCl	Fusion	919.15	915.55	-0.29499	1.003932063	[67]
BaCO ₃	Solid-phase transition	1081.15	1086.95	0.72490	0.996503979	[67]
Ag	Fusion	1234.95	1235.65	0.07273	0.999433497	[67]

After testing known calibrants, KClO₄, Ag₂SO₄, CsCl (solid–solid transition and melting), BaCO₃, and Ag, their average transition temperatures were calculated, with associated errors shown as error bars on the calibration graph. A linear fit

(mean line) was plotted, along with $\pm 2\sigma$ boundaries. All average calibrant values fell within the 2σ range (429.75 K to 1234.95 K), indicating that, for the RbF-UF₄ phase equilibria experiments, the data is accurate to within 95% confidence.

Table S2: TGA-DSC standards reagents nominative properties as given in Netzsch (2008) [67].

Calibrant	Temperature (K)	Enthalpy (kJ mol ⁻¹)	Purity (%)
In	429.6	3.291	99.99
KClO ₄	573.8	14.533	99.9999
Ag ₂ SO ₄	699.2	16.182	99.99
CsCl	749.0	2.896	99.99
BaCO ₃	1081.0	18.727	99.997
Ag	1234.0	11.296	99.99

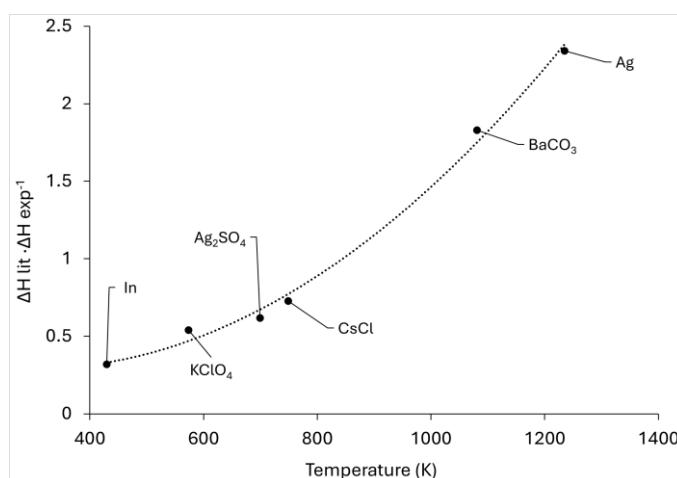


Fig 6: Calibration curve with second order fitting for STA-7200 TGA/DSC

DSC enthalpy calibration followed the Hitachi manual, employing second-order polynomial regression for best fit. A second-order polynomial was used to fit the calibration curve (shown in **Fig. 6**); $\Delta H \text{ lit} \cdot \Delta H \text{ exp}^{-1} = 2.393\text{E-}06 \text{ K}^2 - 1.435\text{E-}03 \text{ K} + 5.055\text{E-}01$. Temperature calibration was performed using indium and silver, ensuring all subsequent melting points fell within range. Validation tests showed solid–solid transitions within ± 1 K of literature values.

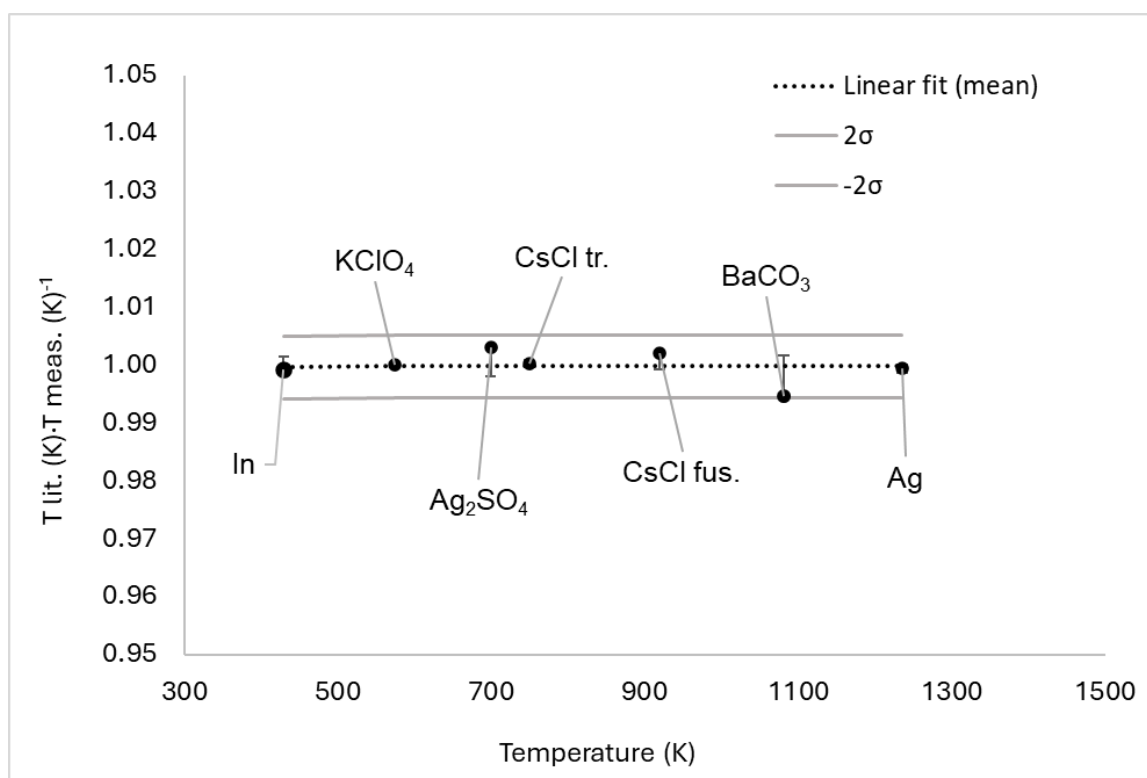


Figure S1: Temperature calibration test of the Hitachi STA7200

The accuracy of the temperature calibration was assessed using the ratio $T_{lit} (K) \cdot \bar{T}_{measured} (K)^{-1}$ across a temperature range of 429.75 K to 1234.95 K. The data show a high degree of consistency, with all measured calibrant ratios falling within a narrow band defined by the $\pm 2\sigma$ bounds: 0.994 (-2σ) and 1.005 ($+2\sigma$). The average linear fit of the ratio across the full temperature range was 0.99977, indicating excellent proportional agreement between measured and literature values. Crucially, the absence of any significant trend in this ratio with increasing temperature confirms that both absolute and relative errors remain effectively constant across the range. This demonstrates that the calibration is accurate and stable at both low and high temperatures and supports a >95% confidence that all recorded measurements fall within $\pm 1-3$ K of their true values.

DSC measurements for RbF-UF₄ provided as supplementary data for Chapter 5: Thermodynamics of the RbF-UF₄ system: a potential fuel candidate for molten salt reactors publication, *Submitted to the Journal of Chemical Thermodynamics*, September 2025

Table S3: Observed DSC thermal events

X (UF₄)	Type of equilibria	Temperature (K)
0.024	Eutectic	978
	Liquidus	1055
0.044	Eutectic	962
	Liquid	1044
0.050	Eutectic	1034
	Liquid	982
0.074	Eutectic	980
0.100	Eutectic	975
0.117	Eutectic	978
	Liquid	1042
0.131	Eutectic	979
0.156	Eutectic	968
	Liquid	1175
0.170	Eutectic	974
	Liquid	1197
0.293	Rb ₃ UF ₇ formation	687
	Peritectic	1064
	Liquidus	1251
0.312	Peritectic	1082
	Liquidus	1196
0.343	Rb ₃ UF ₇ formation	684
	Pre-eutectic	886
	Eutectic	955

	Liquidus	1080
0.380	Rb ₃ UF ₇ formation	684
	Pre-eutectic	880
	Eutectic	953
	Liquidus	1056
0.400	Rb ₃ UF ₇ formation	683
	Unidentified	951
	Eutectic	971
	Liquidus	1025
0.430	Unidentified	785
	Eutectic	952
0.460	Rb ₃ UF ₇ formation	683
	Eutectic	951
	Peritectic	967
	Liquidus	994
0.470	Rb ₃ UF ₇ formation	684
	Eutectic	952
	Peritectic	963
	Liquidus	1000
0.485	Peritectic	962
	Liquidus	1003
0.490	Peritectic	962
	Liquidus	1008
0.500	RbUF ₅ congruent melting	1000
0.505	Pre-eutectic	963
	Eutectic	983
	Liquidus	1008
0.540	Pre-eutectic	962
	Eutectic	985
0.595	Pre-eutectic	963
	Eutectic	982

	Peritectic	999
0.620	Peritectic	999
	Liquidus	1034
0.716	Peritectic	981
	Peritectic	1009
	Liquidus	1118
0.760	Peritectic	1000
	Peritectic	1126
	Liquidus	1161
0.800	Peritectic	1000
	Liquidus	1131
0.840	Peritectic	1011
	Peritectic	1126
	Liquidus	1237