

Extended Summary of the PhD dissertation: *Molten Salt Reactor Chemistry: Structure and Equilibria* by J.A. Ocadiz Flores

Molten salts are a class of ionic liquids which have in recent years been the focus of extensive fundamental research given that they are a versatile class of reaction media with a variety of appealing thermophysical and thermochemical properties (e.g. melting points, heat capacities, vapor pressures, densities, thermal conductivities, etc..) suited for a variety of industrial applications, in particular at high temperature. The most well-known is perhaps the production of materials as important as aluminum and sulfuric acid, yet thermal energy storage is also a notable application. One of the most noteworthy application of molten salts, is as fuel and coolant for a type of nuclear fission reactor known as the Molten Salt Reactor (MSR). In its most general sense, a MSR is a class of nuclear reactor in which fissile ^{235}U , ^{233}U , ^{239}Pu and/or fertile isotopes (e.g. ^{232}Th , ^{238}U) are dissolved in a carrier salt. The resulting mixture acts both as fuel and coolant. The two prototypes which have been built in the past used a fluoride fuel, so historically most work has concentrated on fluoride salt mixtures. However, modern day reactor developers are also interested in chloride fuels, so both molten salt fuel families are relevant at present.

Due to the nature of the fission reaction, MSR fuel is a mixture with considerable chemical complexity, comprising a multi-component salt solution, noble gases, and noble metal precipitates. A thermodynamic description of this complex system must be the foundation of any systematic attempt to select its original composition, predict its behavior in the reactor core during normal operation and accidental conditions, (in particular predict liquidus temperature, precipitation of a given component, stability of structural materials against the fuel), and guide reprocessing schemes after burn-up. In practice, this must be done by dividing the whole system into smaller building blocks for which a very accurate analysis can be provided: first unitary systems, then binary, ternary, and so on. The Gibbs energy is the thermodynamic potential which indicates which phase or combination thereof will be stable at a given composition and isothermal-isobaric state: that which minimizes the total Gibbs energy of the system. Thus every level of description should minimally contain the set of phases involved (end-members, stoichiometric intermediate compounds, solid and liquid solutions) and the Gibbs energy associated with each one.

Solution phases will have a Gibbs energy corresponding to the weighted sum of the Gibbs energies plus a mixing contribution. The mixing contribution in turn will consist of an ideal term arising from the configurational entropy, and an excess term which will be zero if the solution is ideal and non-zero otherwise. In general this excess term is unknown and needs to be optimized, along with any other Gibbs energy functions which may be unknown, so as to reproduce known thermodynamic data. This optimization is at the core of thermodynamic modelling. Closely related to the excess Gibbs energy of the liquid solution is the local structure, which for molten salts may be ionic, molecular, or polymeric, and which will also be manifest in excess contributions to the mixing enthalpies and entropies, heat capacities, activities, and other thermophysical properties. As density and viscosity are state functions, they may in principle also be linked to the Gibbs energy of the system and to the local structure.

This dissertation is an effort in the direction of making an explicit link between the structure, thermodynamics, and state properties (density, viscosity) for a set of salts comprised of alkali actinide halides related to MSR technology: ACl-ThCl_4 ($A = \text{Li, Na, K}$), LiF-AnF_4

(An = Th, U), NaF-ThF₄, KF-ThF₄, NaCl-UCl₃, and the ternaries LiF-ThF₄-UF₄, LiF-KF-ThF₄, and NaF-KF-ThF₄. Several experimental and computational techniques were used throughout this work to achieve said goal: differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermal relaxation calorimetry, X-ray absorption spectroscopy (XAS), molecular dynamics (MD), and density functional theory (DFT). The collected data were modelled simultaneously with computational thermodynamics, using the so-called CALPHAD method (Calculation of Phase Diagrams).

A thermodynamic assessment of the KF-ThF₄ binary system using the CALPHAD method is reported initially, in which the liquid solution is described by the modified quasichemical formalism in the quadruplet approximation. The optimization of the phase diagram is based on experimental data reported in the literature and newly measured XRD and DSC data, which allowed to solve discrepancies between past assessments. The low temperature heat capacity of α -K₂ThF₆ was also measured, using thermal relaxation calorimetry; from these data the heat capacity and standard entropy values were derived at 298.15 K and implemented in the model. Taking existing assessments of the relevant binaries, the new optimization was moreover used to assess the ternary systems LiF-KF-ThF₄ and NaF-KF-ThF₄, for which novel DSC data were also collected. The standard enthalpy of formation and standard entropy of KNaThF₆ were re-calculated from published e.m.f data, and included in the assessment of the ternary system.

Since chloride salts are also candidates for MSR fuels, a thermodynamic investigation of the ACl-ThCl₄ (A = Li, Na, K) binary systems was furthermore carried out. The excess Gibbs energy of the liquid solutions was also described using the quasi-chemical formalism in the quadruplet approximation. The phase diagram optimizations in this case were based solely on the experimental data available in the literature. The thermodynamic stability of the liquid solutions increases in the order Li < Na < K, in agreement with simplified interactions and structural models.

To develop realistic structural models, the short-range structures of AF-AnF₄ (A = Li, Na, K, Cs; An = Th, U) systems were then probed using *in situ* high temperature Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Notably, the EXAFS spectra of pure molten ThF₄ and UF₄ were measured for the first time. The data were interpreted with the aid of MD simulations and standard fitting of the EXAFS equation. As in related studies, a speciation distribution dominated by [AnF_x]^{4-x} (x = 7, 8, 9) coordination complexes was observed. The average coordination number was found to decrease with the increasing size of the alkali cation, and increase with AnF₄ content. An average coordination number close to 6, which had not been detected before in melts of alkali actinide fluorides, was seen when CsF was used as solvent.

Using MD, the structures of the melts were further characterized for composition and temperature domains extended beyond what was possible with the EXAFS technique, for the systems LiF-UF₄ and NaF-ThF₄, which were taken as case studies for the implementation of an advanced quasi-chemical formalism. For both binary systems the phase diagram equilibria were explored with XRD and DSC. The densities, excess molar volumes, thermal expansion, heat capacities, and enthalpies of mixing were moreover extracted from the MD simulations across a range of temperatures and compositions. The distributions of heteropolyanions in the liquid solution were also calculated, and modelled using the quasi-chemical formalism in the

quadruplet approximation, thereby explicitly linking the structural and thermodynamic properties to result in a rigorous physical description of the melts. The existence of 7- and 8-coordinated single-shell complexes and of the dimeric species $[\text{U}_2\text{F}_{14}]^{6-}$ (in the case of LiF-UF₄) and $[\text{Th}_2\text{F}_{13}]^{5-}$ (in the case of NaF-ThF₄) were taken into account. Subjecting the optimization of the excess Gibbs energy parameters of the liquid solution to the constraints of the phase diagram data and local structure of the melt as derived from the EXAFS and coupled MD simulations, a CALPHAD-type assessment was proposed, linking structural and thermodynamic properties, with a rigorous physical description of the melt. For NaF-ThF₄, the description was made even more rigorous by experimentally deriving the standard entropies from low-temperature heat capacity measurements of two phases appearing in the system, with formula Na₂ThF₆ and NaTh₂F₉. Furthermore, the low and high-temperature heat capacities of these phases were successfully bridged with a methodology combining DFT and the Quasi-Harmonic Approximation (QHA).

Finally, an effort was made to compute the density and viscosity functions, in a way consistent with the thermodynamic assessments. Models for four systems were optimized: NaCl-UCl₃, LiF-ThF₄, LiF-UF₄, and LiF-ThF₄-UF₄. Assessment of all four systems, using the modified quasichemical formalism in the quadruplet approximation for the description of the liquid solutions, were carried out. In the case of NaCl-UCl₃, phase diagram and mixing enthalpy data available in the literature were incorporated. For the fluoride systems, recently published data on some solid phases were taken into account, while retaining the most recently published descriptions of the liquid solutions. The densities of the liquid solutions, when not ideal, were modelled using pressure-dependent terms of the excess Gibbs energy, while the viscosities were modelled using an Eyring equation.

In its concluding remarks, the dissertation recommends four further lines of enquiry. First, expanding the existing thermodynamic database to include more alloy-salt interactions, given that corrosion is a central phenomenon in fluid fuel reactors. Second, curating a database of MD potentials to be used alongside thermodynamic databases, since expert use of MD can have a very useful role as a source of high quality data. Third, proposing electrical and thermal conductivity models analogous to the density and viscosity models elaborated in the work. Fourth, identifying the salts belonging to a hypothetical minimum significant set (MSS) needed to describe real salt fuel accurately without meeting the strong requirement of describing all thermodynamic interactions, as these scale combinatorially.

Overall, the thesis improves the state of knowledge on the topology of the phase diagrams studied. Throughout the work, structural motifs of actinide-bearing molten salts are discussed, with a view to aid in the prediction of the characteristics of systems which are to this date unexplored. The quasi-chemical formalism has become well-established in the computational thermodynamics of MSR chemistry, and the number of systems assessed is already substantial. This work is a template showing how databases of molten salt fuels may be extended to reflect more largely structure, density, and viscosity in combination with the thermodynamic properties.