Article

Developing Practical Models of Complex Salts for Molten Salt Reactors

Theodore M. Besmann [1,*] and Juliano Schorne-Pinto [2]

[1]   Nuclear Engineering Program, University of South Carolina; besmann@sc.edu
[2]   Nuclear Engineering Program, University of South Carolina; julianos@mailboxsc.edu
*   Correspondence: besmann@sc.edu

Abstract: Molten salt reactors (MSRs) utilize salts as coolant or as the fuel and coolant together with fissile isotopes dissolved in the salt.   It is necessary to therefore understand the behavior of the salts to effectively design, operate, and regulate such reactors, and thus there is a need for thermodynamic models for the salt systems.   Molten salts, however, are difficult to represent as they exhibit short range order that is dependent on both composition and temperature.   A widely useful approach is the modified quasichemical model in the quadruplet approximation that provides for consideration of first and second nearest neighbor coordination and interactions.   Its use in the CALPHAD approach to system modeling requires fitting parameters using standard thermodynamic data such as phase equilibria, heat capacity, and others.   Shortcoming of the model is its inability to directly vary coordination numbers with composition or temperature.   Another issue is the difficulty in fitting model parameters using regression methods without already having very good initial values.   The proposed paper will discuss these issues and note some practical methods for the effective generation of useful models.

Keywords: Thermodynamic modeling, CALPHAD, molten salt, molten salt reactor, thermodynamic database, modified quasichemical model, fluoride salt, chloride salt, salt system

1. Introduction

The turn of the 21st century saw the return of interest in molten salt reactor (MSR) systems after more than three decades, as noted in the roadmap efforts at the Generation-IV International Forum in 2002.[1]   There is now several nations with enterprises underway to develop and deploy molten salt fueled, or solid fuel and molten salt cooled, reactor systems, although at this writing none have yet entered the prototype stage.   The previous successful effort was the Molten Salt Reactor Experiment (MSRE), a demonstration program at Oak Ridge National Laboratory that operated between 1965 and 1969.   The reactor was an 8 MWt critical system operating with LiF-BeF_2-ZrF_4-UF_4 flowing through a graphite moderator at ~650°C.[2]

The worldwide interest in MSRs encompasses a broad range of concepts that manifest as differing salt compositions.   These vary from thermal reactors fueled/cooled with $66LiF$-$34BeF_2$ mol%, known as FLiBe to those for fast reactors with $46.5LiF$-$11.5NaF$-$42KF$ mol% known as FLiNaK. As in most concepts, the coolant also contains the fuel, and these systems or their compositional variants will host dissolved fissile and fertile actinide fluorides.   Chloride-based systems, reserved for fast reactors as the heavier fuel/coolant elements make thermalizing neutrons difficult, typically include $LiCl$-$NaCl$-$MgCl_2$ compositions, which for fuel host fissile actinide chloride(s).

The exceptionally valuable MSRE experience emphasized how important is the ability to understand and control the dynamic (temporal and spatial) evolution of salts in a reactor.   The sources of such variation are

*   Burnup-generated fission product (FP) and transuranic (TRU) elements
*   Addition of fresh fuel salt

- Evolving composition due to fission/isotopic decay/neutron absorption
- Graphite pickup (where salt directly contacts graphite moderator) and reaction
- Corrosion product dissolution/deposition
- In-leakage of contaminants (atmospheric oxygen and nitrogen)
- Adjustment of redox with halide addition
- Removal of dissolved/suspended fission and corrosion products, and TRU elements
- Off-gas removal
- Local and cycle temperature

The high temperature environment of the fuel/cooling loop of a MSR and the nature of the phases (largely ionic liquids and solids together with gases/vapors, metals, and graphite), is expected to drive chemical and phase behavior toward equilibrium, and thus are governed by their thermodynamic properties, i.e., the Gibbs energy. Even when the effects of radiation and kinetics, i.e., non-equilibrium phenomena, are controlling, knowledge of the equilibrium state provides limits of phase stability and ultimate chemical potential. Thus, the computed equilibrium state of the molten salt fuel/coolant can provide knowledge about

- Local composition/speciation
- Precipitating solid phases
- Liquid-liquid immiscibility
- State of dislodged graphite or alloy material
- Chemical potentials/redox related to corrosion behavior and transport
- Vapor pressures
- Thermal expansion/specific volume
- Input for phase field calculations: Modeling reactions, nucleation, and grain growth
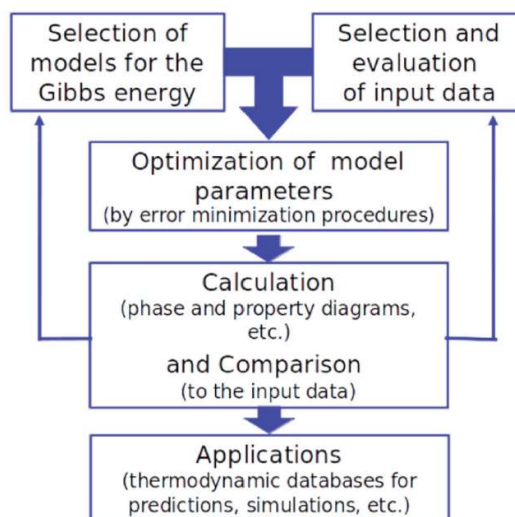- Energetics for potentially computing viscosity

The path forward in developing thermal properties of MSR salt systems has emerged within a number of national programs, which for the U. S. can be seen in a current roadmap document.[3] As noted in the roadmap, a thermodynamic database focused on MSR modeling needs, the *Molten Salt Thermal Properties Database-Thermochemical* (*MSTDB-TC*) [4], is being developed and available to users. It joins other efforts such as the JRCMSD [5] and commercial databases such as the SGTE Molten Salt Database [6] as international resources. Common to these efforts is the effective use of the CALPHAD (CALculation of PHAse Diagrams) [7,8] approach to generate coherent sets of Gibbs functions/models that accurately predict phase equilibria and constituent chemical potentials, the process for which is described in Figure 1.
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2. Solution Models for Salt Systems
The relevant phases in MSR fuel/cooling loops involve both salts and non-salts, and a complete understanding of behavior requires having Gibbs energy functions for all phases. For the salts, these include the melt as well as solid phases and vapor species. This is true not only for the base salts noted above, but also include important fission and corrosion products, and TRU elements. Materials of construction, such as the alloys of piping and components that contact the salt, also need to be represented to assess potential for interactions. Noble metal fission products generated in the nuclear processes will not form salts nor have significant solubility in the salt melts, and thus models for their alloy phases are needed to understand their behavior in the MSR fuel loop. Finally, Gibbs functions for important gaseous species are needed to predict vapor pressures for in situ fuel processing/off-gas treatment and safety analyses. Of the various types of phases here noted, all but the salt systems have fairly straightforward solution models for non-stoichiometric crystalline and liquid phases that are applied widely across many material

systems.   The ionic crystalline salt phases with varying stoichiometry are also relatively easy to represent with standard sublattice models for solution phases.   It is salt melts that have historically been very challenging to accurately represent and are the subject of the current work.

Figure 1.   Scheme for performing CALPHAD assessments for system thermodynamic representa-

tions.[7,8]

The difficulty in using standard thermochemical models for molten salts is their tendency to exhibit short range order (SRO).   Capturing the influence of this tendency as a function of temperature and composition requires representing the energetics beyond the nearest neighbor atoms and their coordination.   The effect can be seen in *in situ* studies of molten salts, such as EXAFS, and the results from molecular dynamics calculations.[9–12]   Means for addressing these issues have been developed as they are common to systems beyond salts.   Pelton and Blander [13] noted that SRO is observed in alloy liquids that are combinations of relatively electropositive and electronegative metals (e.g., Cu-Au, Mg-Bi, and Li-Pb), and to a great extent in silicate-containing systems via the formation of orthosilicate ions, as well as in salt systems.
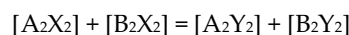
Ideally, it is possible to compute molten salt behavior using atomic scale methods such as *ab initio* molecular dynamics (AIMD), as demonstrated by Nguyen *et al.* [14].   In principle, one could eventually compute the behavior of many-element systems, however, even simple pseudo-binaries such as LiCl-KCl are computationally costly to fully describe making the widespread use of AIMD impractical.   An early, mesoscale approach used for the SGTE Molten Salt Database [15] effort is the two-sublattice ionic liquid model[6], which while allowing interaction among species on a fictive cation and anion sublattice, thus considering charge balance, does not address the influence of SRO. Another concept is that of associate species.[16,17]   Essentially, SRO is represented by a mixture of complex liquid species in addition to the endmember components. These typically mimic the stoichiometry of stable crystalline phases in the system, as the concept makes the reasonable assumption that any SRO will be due to molecular clusters similar in stoichiometry to the solid phases.   The energetics are found through appropriate choice of these associate species and adjusting their Gibbs formation energy to provide a fit to the system phase equilibria.   Pelton[18] notes that the approach is problematic as it cannot be applied to systems exhibiting positive deviations from ideality and the results of extending models to higher order systems are often poor.

A marked improvement in modeling systems with SRO is based on the quasichemical theory of Guggenheim[19], which more directly addresses species coordination within
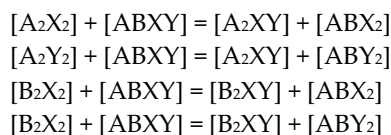
melts. The approach can appropriately address the steep minimum in mixing enthalpy as a function of composition (forming a deep eutectic) and similarly the bimodal mixing entropy due to SRO. It thus avoids the use of computationally prohibitive AIMD and the limitations of models such as the associate species. Pelton and Blander[13] adapted the quasichemical scheme such that minima in mixing enthalpy and entropy are not fixed at 50% composition as required by the Guggenheim theory, making for a more realistic approach. Pelton and coworkers have substantially expanded on the technique over the years which can now address complex reciprocal salts with a modified quasichemical model in the quadruplet approximation (MQMQA).[18,20–23]

2.1. Modified Quasichemical Model

A description of the governing relations for the MQMQA would be redundant with other excellent reviews, yet it is worthwhile to describe its working concepts. A reciprocal salt has two cations (A & B) and two anions (X & Y) and these can exhibit SRO as first nearest neighbors (FNN) and second nearest neighbors (SNN), which are cation-anion and cation-cation/anion-anion, respectively. These can be represented by quadruplets, allowing reciprocal reactions for FNNs

$$[A_2X_2] + [B_2X_2] = [A_2Y_2] + [B_2Y_2]$$

and for SNNs

$$[A_2X_2] + [ABXY] = [A_2XY] + [ABX_2]$$
$$[A_2Y_2] + [ABXY] = [A_2XY] + [ABY_2]$$
$$[B_2X_2] + [ABXY] = [B_2XY] + [ABX_2]$$
$$[B_2X_2] + [ABXY] = [B_2XY] + [ABY_2]$$

One can assign a Gibbs energy of formation to each of the quadruplets which then allows for managing their interactions.

While the MQMQA addresses reciprocal salts, MSR applications generally utilize a single anion, fluorine or chlorine. (The exception would be in dealing with the iodine fission product whose behavior is important to understand in performing accident analyses.) For the same anion systems, the MQM simplifies to the pair exchange reaction for FNNs

$$[A_2X_2] + [B_2X_2] = 2[ABX_2]$$
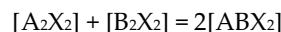
where the exchange Gibbs energy, $\Delta G_{AB/X}$ is related to the pair formation and in this approach is expanded in a polynomial representing interactions among the components, which are related to parameters dependent on the cation-cation pair fractions. These are generally empirically determined via fitting the model to data.

For salt melts the relationship between maximum SRO, and thus the most negative heat of mixing, is represented by the cation-cation coordination numbers $Z^A_{AB/XX}$ and $Z^B_{AB/XX}$. These are used to impose the condition of charge-neutrality, such that

$$\frac{q_A}{Z^A_{AB/XX}} + \frac{q_B}{Z^{AB}_{AB/XX}} = \frac{q_X}{Z^{AX}_{AB/XX}} + \frac{q_X}{Z^X_{AB/XX}}$$

where q_i are the absolute values of the cation and anion charge on i. The relation also allows the cation-cation coordination numbers to define the values for the anion-anion coordination numbers.

2.2. Determining Coordination Numbers

As can be appreciated from the MQM relations, the choice of coordination numbers, which are fixed for each component, can be important for obtaining accurate models of salt melts. The values are typically selected from observation of the composition at the greatest SRO and minimum in heat of mixing, or mixing enthalpy. For salts and similar systems, these can be related to eutectic and crystalline phase composition, as these correspond to Gibbs energy minima.

The use of fixed coordination numbers across the entire composition of a salt typically obtained from phase stoichiometries and charge has been common. Unfortunately, in more complex systems where one or more cations have a charge >1 and the pseudo-binary phase diagram has more than one eutectic, it is apparent that the coordination in the melt is varying. Ultimately, the choice of the single set of coordination numbers will, in those cases, prevent the resulting MQM relations from accurately representing the melt across all compositions.

2.3. Coordination Numbers and MQM Generation

The issue of variable coordination numbers is illustrated in a comparison of analyses performed with and without that assumption. An analysis of fluoride fuel salt for MSR applications by Benes and Konings[24] reasonably well reproduces the experimental phase diagram for the pseudo-binary NaF-BeF$_2$ using measurements confined to less than 60 mol% BeF$_2$. Their MQM representation utilized single endmembers for the fluorides and thus the fixed coordination numbers

$$Z_{NaBe/FF}^{Na} = 3$$
$$Z_{NaBe/FF}^{Be} = 6$$

with that for F-F equal to 3.

A later effort on the NaF-BeF$_2$ pseudo-binary by Robelin and Chartrand[25] endeavored to extend the application of the MQM with variable coordination numbers by adopting two endmembers for BeF$_2$, which they identified as Be$_{IV}$F$_2$, the four-coordinated beryllium with fluorine, and the dimer Be$_2$F$_4$. These yielded still better agreement with the observed higher BeF$_2$-content phase equilibria by allowing compositions to be computed with coordination numbers intermediate between the monomer and dimer determined by the ratio of these endmembers. The values adopted for each of the endmembers were

$$Z_{NaNa/FF}^{Na} = 6; \quad Z_{NaNa/FF}^{F} = 6$$
$$Z_{BeIVBeIV/FF}^{BeIV} = 4.8; \quad Z_{BeIVBeIV/FF}^{F} = 2.4$$
$$Z_{Be2B\quad/FF}^{Be2} = 6; \quad Z_{Be2Be\quad/FF}^{F} = 1.5$$
$$Z_{NaBeIV/FF}^{Na} = 3; \quad Z_{NaBeIV/FF}^{BeIV} = 6$$
$$Z_{NaBeIV/FF}^{Na} = 3; \quad Z_{NaBeIV/FF}^{BeIV} = 6$$
$$Z_{NaBe\quad/FF}^{Na} = 2; \quad Z_{NaBe\quad/FF}^{Be} = 6$$

These yielded an improved fit to the system and thus an improved reproduction of the entire phase diagram (Figure 2). The variation in concentration of Be$_{IV}$F$_2$ and Be$_2$F$_4$ is shown in the inset in the phase diagram of Figure 2. In the current work, it is likely that additional endmembers will be needed for uranium-containing systems and systems with ZrF$_4$ as well. While other MSR salt constituents will have valences >1 and yield more

complex pseudo-binary phase diagrams, they will be present at low concentrations and therefore the use of variable coordination numbers will likely not be warranted.
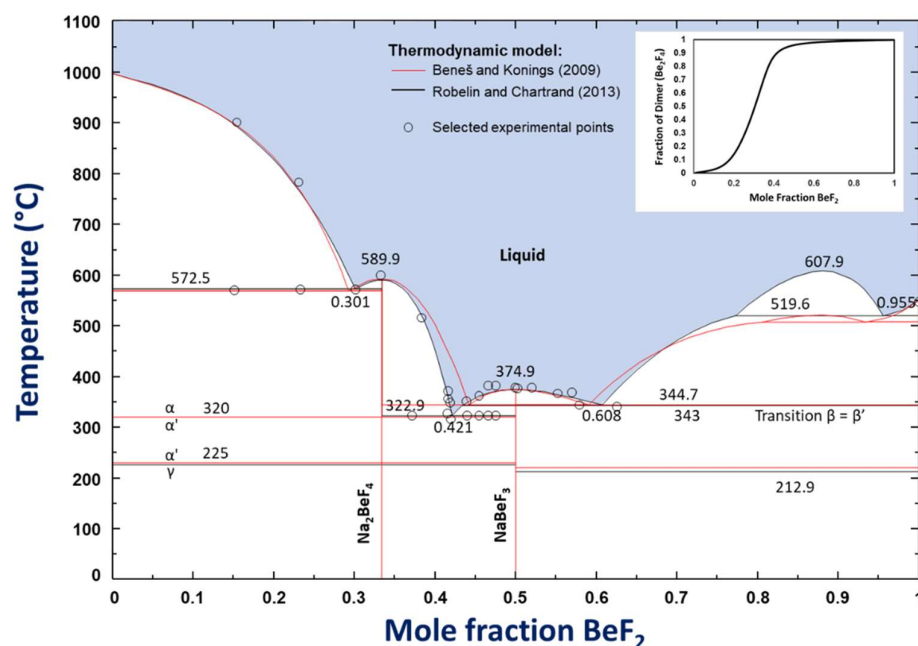

Figure 2. Overlaid phase diagrams based on melt models for NaF-BeF2 using[25] and not using[24] multiple endmembers for BeF2. The selected experimental data points are those of Roy, et al. *[26]* and Novoselova *[27]*. The inset indicates the relative concentration of the monomer and dimer of BeF2 at 850°C based on the Robelin and Chartrand*[25]* MQM representation.

3. Performing System Assessments for Salts

The term used to describe the comprehensive analysis of a system to obtain a fully representative set of Gibbs functions and models is an assessment. Sets of the thermochemical relations for phases and vapor species in a system constitute its full description and can be used with a global energy minimization routine to determine the equilibrium state of phases at a fixed temperature, pressure, and composition. The self-consistent set of Gibbs functions accurately describe the phase equilibria and characteristics of the phases in the systems. Following the CALPHAD approach (Figure 1), multiple sources and types of information are used in optimizations of model parameters for Gibbs function relations. Put simply, all relevant, reliable, consistent, and acceptably accurate values for determining thermodynamic functions that have been measured, estimated, or computed from first principles are used to fit parameters of Gibbs functions. These include those that represent interactions among components in solid and liquid solutions, which include variable stoichiometry solid phases. The process for integrating the information and the fitting methodology (regression analysis) is termed optimization. When the results of the optimization allow the determined Gibbs functions to be used in global energy minimization calculations (the computing of equilibria) that reproduce the known phase equilibria (diagrams) and other characteristics (e.g., elemental chemical potentials), then the process has been successful.

There are two overriding issues, however, that can cause system optimizations to be difficult or impossible. The first is the lack of sufficient, consistent, and accurate data that will allow successful fitting to Gibbs functions and solution models. The second is the difficulty in performing a regression analysis to fit often disparate types, or even the same type of data to a model, whether for a variable stoichiometry solid phase (e.g., sublattice

model) or liquid (e.g., MQM).   The solution to the first problem is the obvious generation of the required data by appropriate means.   The solution to the second problem, however, has yet to be fully resolved.   It is possible to have an adequately complete and accurate set of information to allow, for example, the fitting of MQM parameters for a salt melt, including Gibbs functions for crystalline phases, to well-reproduce the system phase equilibria, yet have great difficulty with obtaining parameters from a successful regression analysis.   Even for the simpler systems where variability in coordination numbers is not an issue, it can be difficult to obtain a successful fit to solution models.

Currently, there is no widely available solution to the problem of easily performing regression analysis for more complex solution models, and particularly for MQM.   It has always been something of an art to fit data to successfully optimize a system for more than very simple systems and models.   It has depended on a close understanding the likely behavior of a system, with the goal of successfully reproducing behavior with a minimum number of parameters. Tools such as the optimization modules in the FactSage™ [28] and Thermo-Calc [29] software suites offer the promise of being helpful, however, the optimizations to be successful generally require initial estimates for the regression analysis that are not far from the eventual final values.   Obviously, this severely decreases the value of these routines.

4. Higher Order Systems and Example Applications

There are a significant number of assessed pseudo-binary salt systems of interest for MSRs, however, models for melts with multiple components will be needed that reflect the complexity of salt compositions.   The base systems for fuels salts such as FLiBe, FLiNaK, and LiCl-NaCl-MgCl$_2$, will also contain some concentrations of the same halide actinide. Thus, a MQM addressing systems with at least four component halides will be required to well represent MSR salts.   In addition, the nuclear processes of a reactor generate ~60 different elements as fission products or transuranics, albeit ranging from low concentrations to trace amounts. There are also corrosion products or contaminant elements that dissolve in the salt. Given this potentially large number of constituents the task of obtaining solution descriptions that include all possible interactions among all the components, in principle, would be impossibly large.   The effort becomes tractable, however, as it is statistically apparent that the low concentration elements will be proximate almost solely with, and thus solely energetically interact with, the major fuel salt constituents obviating the need for addressing very large numbers of interactions.   There thus remains a substantially more restricted set of systems to be addressed. The MQM can accommodate multiple components, with the expressions well described by Pelton [18]. These require interpolation from lower order systems, and examples of which are becoming more common as attempts to represent more complex systems expand.

An example of a set of interpolated systems is seen in the five endmember LiF-BeF$_2$-UF$_{3,4}$-PuF$_3$ system developed for the MSTDB-TC.   The types of information that can be generated from such models can be seen in Figure 3a, which illustrates computed liquidus projections for the LiF-BeF$_2$-UF$_4$ where all composition additionally contains 10 mol% UF$_4$ and 1 mol% PuF$_3$.   For example, it is clear that the actinide content markedly increases the salt melting point from that of FLiBe of 456°C, with an actinide salt solid solution the first precipitating phase.   A closer look at the effect of actinide fluorides is seen in Figure 3b, which reflects the significant increase in liquidus temperature particularly due to the presence of PuF$_3$.

Adjustment of the UF$_3$-UF$_4$ ratio in MSR systems is expected to be used to control fluorine potential, and therefore the propensity for a corrosive attack of structural alloys and the vapor pressure of some species.   That type of critical information is also available

from these kinds of thermochemical models, as seen in Figure 4 which provides 750°C computed, RT $\ln(p_{F2})$ values for FLiBe containing 10 mol% UF_x as a function of UF_3/UF_3 ratio. On the plot are also indicated the RT $\ln(p_{F2})$ values for equilibria between the major Hastelloy-N elements (71Ni-16Mo-7Cr-4Fe mass) and their fluorides (except for molybdenum, which has values that are significantly more positive). Accurate calculations also require consideration of the activities of the metals in the alloy, i.e., alloy solid solutions or secondary phases, and thus models for the alloy phases (SGTE 2020 Alloy Database) [24] were equilibrated with the salt in calculating the indicated equilibrium reactions of Figure 4. The metal-fluoride equilibria thus provide threshold values, where more positive system RT $\ln(p_{F2})$ values will cause the fluoride of the metal to be more stable and thus potentially corrosion of the alloy. The understanding that the mechanism of corrosive attack in nickel alloys is the fluoriding and dissolution of chromium is again made apparent in the results in Figure 4 where the reaction $[Cr]_{H-N} + F_{2\,(g)} = CrF_{2\,(l)}$ occurs at the most negative values of RT $\ln(p_{F2})$ among the alloy constituents.

(a)   (b)
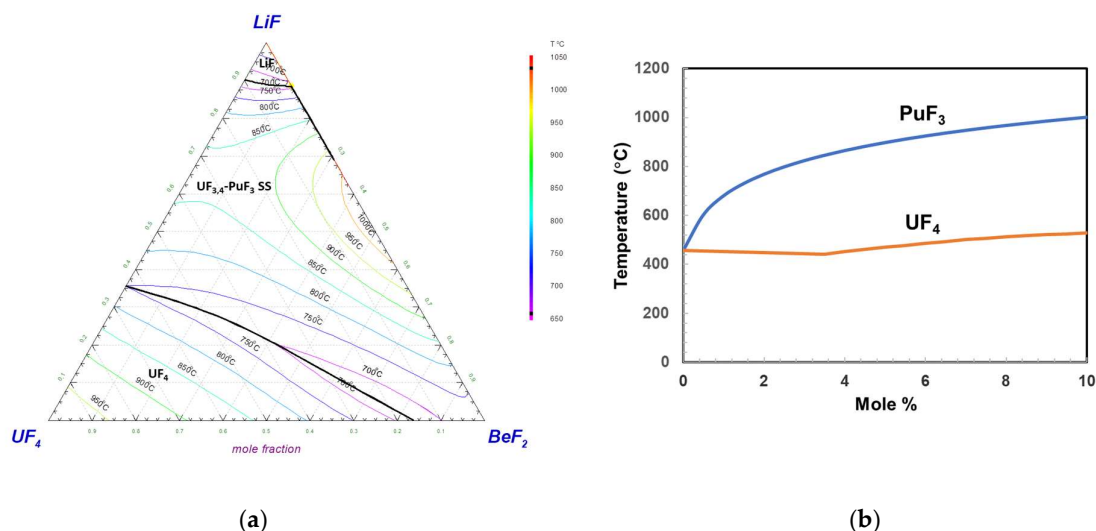
Figure 3. The models for the LiF-BeF2-UF4 -UF3-PuF3 system of *MSTDB-TC* [4] were used to (a) compute the liquidus projections for the pseudo-ternary LiF-BeF2-UF4 phase diagram with fixed content of 10 mol% UF3 and 1 mol% PuF3 (labeled phase regions indicate the first precipitating phase) and (b)   demonstrate the influence on the liquidus temperature of FLiBe of added components such as UF4 and PuF3.
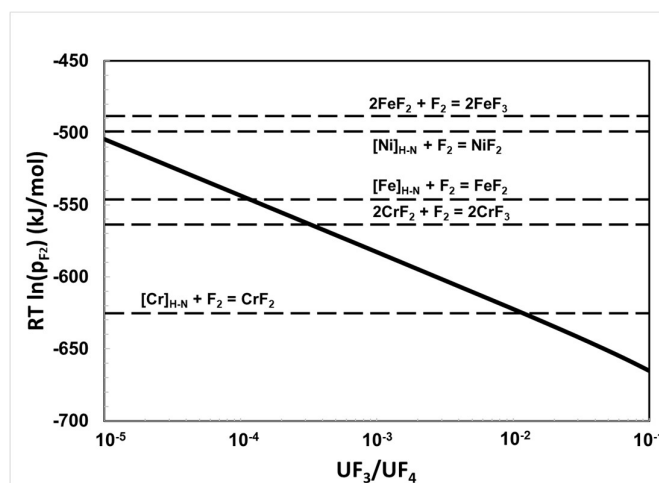

Figure 4.   Computed RT $\ln(p_{F2})$ values at 750°C, for FLiBe containing 10 mol% UF_x as a function of UF3/UF4 ratio together with those for the equilibria between Hasteloy-N elements (71Ni-16Mo-7Cr-4Fe mass) and their fluorides.

5. Conclusions

Thermochemical representations of MSR salt systems are key components for the modeling and simulation of reactor systems. Yet, having a practical model for the salt melt is a significant challenge given the issues of accommodating SRO that includes variation in species coordination over large ranges of temperature and composition, and facilitating interpolation to higher order systems.   Simple solution models do not capture the effect of SRO, and approaches such as AIMD are not practical given unknowns, high computational costs, and inadequate levels of accuracy.   The MQM has offered an extremely useful compromise in that although it does not incorporate all the complexity of salt melt structures, it provides a sufficient framework to include variation in the energetics of the salt and uses a simplified, but adequate view of structure in the melt. This capability together with its treatment of structure with endmember building blocks has allowed the reproduction of many-element system behavior. Generating MQM relations, however, involves understanding potential SRO variations in a system and knowing when it is necessary to add the complexity of multiple same-element endmembers.   Salt melt MQMs coupled with those for intermediate compounds and solid solutions have successfully reproduced phase equilibria and thermochemistry, and has made possible the generation of complex melt databases, including the current *MSTDB-TC*.[4]

In the current work Potential applications of salt system models were briefly explored, including compositional dependence of liquidus temperature and the potential for salt attack on a nickel-based alloy for use in proposed MSRs.   The latter, in particular, demonstrates how salt thermochemical models used together with the understanding of other material systems, in this case Hastelloy-N, can offer guidance with regard to reactor design and operation.   It is envisioned that this thermochemical capability coupled with modeling and simulation codes for salt corrosion will provide for an ultimate ability to predict the stability of reactor materials.

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