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Status of the molten salt thermodynamic database, *MSTDB*

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Aug. 16, 2019

OAK RIDGE NATIONAL LABORATORY
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Advanced Reactor Technology Molten Salt Reactor Campaign

Status of the salt thermodynamic database, MSTDB

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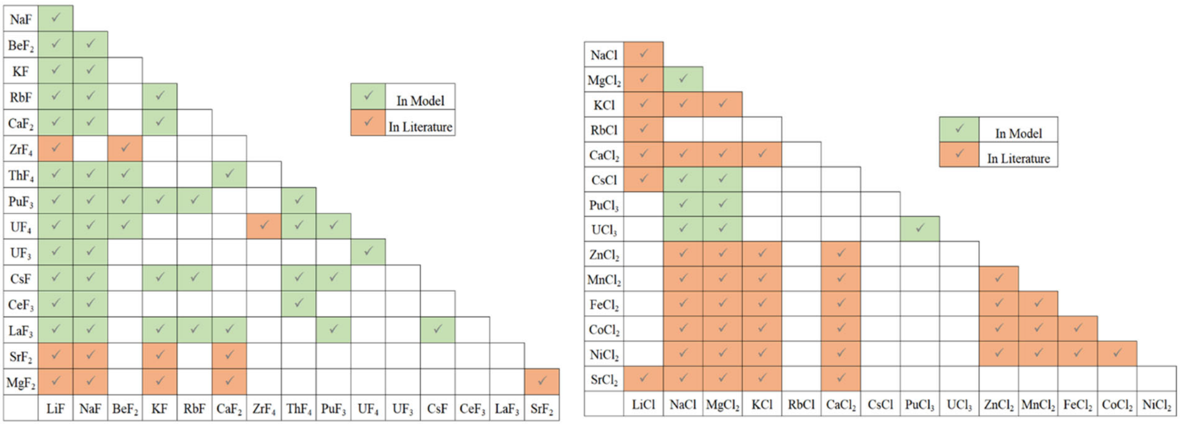
ABSTRACT

The CALculation of PHAsed Diagram (CALPHAD) approach to thermodynamic assessments was used to develop the 1st generation Molten Salt Thermodynamic Database, or MSTDB. It currently contains 21 elements with models for 54 molten salt binary solutions, 26 ternary molten salt solutions, 14 solid solutions, and 140 multicomponent, stoichiometric compounds. The effort continues with the aim of extending MSTDB to include all the elements that will exist during operation of a molten salt reactor to model the thermochemical behavior with burnup along with additives and corrosion products.

1. INTRODUCTION

The Department of Energy Advanced Reactor Technology Molten Reactor Program aims to use the CALculation of PHAsed Diagram (CALPHAD) approach [1] of thermodynamic assessments[1] to develop a Molten Salt Thermodynamic Database, or *MSTDB*, that incorporates fission and activation products, additives, and other species, e.g. those that might be incorporated into a salt system due to corrosion reactions. The MSTDB should be viewed as a collection of thermodynamic models that are developed from experiments or lower length scale computation that is available for coupling to other modeling and simulation (mod-sim) codes for broad based MSR performance predictions. The overarching aim of the program is to model important phenomena in MSRs with a physics-based approach to support design, operation, and licensing of molten salt reactors. The report describes the status of the MSTDB which currently contains 21 elements with models for 55 molten salt binary solutions, 26 ternary molten salt solutions, 5 higher order liquid solutions (up to 7 components), 14 solid solutions, and 140 multicomponent, stoichiometric compounds.

The status of the fundamental pseudo-binary subsystems for the fluorides and chlorides are shown in Figure 1 below. The green boxes symbolize that the system is already included in the current version of MSTDB while orange boxes indicate that the system is either already assessed in the literature or that sufficient data is available to develop the models for all the phases in that system. Many pseudo-ternary systems summarized in Appendix A are also in MSTDB. However, from Figure 1, it is clear that basic research is needed to populate the fundamental data set needed to define the missing subsystems illustrated as blank or white boxes.



	LiF	NaF	BeF$_2$	KF	RbF	CaF$_2$	ZrF$_4$	ThF$_4$	PuF$_3$	UF$_4$	UF$_3$	CsF	CeF$_3$	LaF$_3$	SrF$_2$
NaF	🟩 ✓														
BeF$_2$	🟩 ✓	🟩 ✓													
KF	🟩 ✓	🟩 ✓													
RbF	🟩 ✓	🟩 ✓		🟩 ✓											
CaF$_2$	🟩 ✓	🟩 ✓		🟩 ✓											
ZrF$_4$	🟧 ✓		🟧 ✓												
ThF$_4$	🟩 ✓	🟩 ✓	🟩 ✓			🟩 ✓									
PuF$_3$	🟩 ✓	🟩 ✓	🟩 ✓	🟩 ✓	🟩 ✓			🟩 ✓							
UF$_4$	🟩 ✓	🟩 ✓	🟩 ✓				🟧 ✓	🟩 ✓	🟩 ✓						
UF$_3$	🟩 ✓	🟩 ✓								🟩 ✓					
CsF	🟩 ✓	🟩 ✓		🟩 ✓	🟩 ✓			🟩 ✓	🟩 ✓						
CeF$_3$	🟩 ✓	🟩 ✓						🟩 ✓							
LaF$_3$	🟩 ✓	🟩 ✓		🟩 ✓	🟩 ✓	🟩 ✓			🟩 ✓			🟩 ✓			
SrF$_2$	🟧 ✓	🟧 ✓		🟧 ✓		🟧 ✓									
MgF$_2$	🟧 ✓	🟧 ✓		🟧 ✓		🟧 ✓									🟧 ✓

🟩 ✓	In Model
🟧 ✓	In Literature

	LiCl	NaCl	MgCl$_2$	KCl	RbCl	CaCl$_2$	CsCl	PuCl$_3$	UCl$_3$	ZnCl$_2$	MnCl$_2$	FeCl$_2$	CoCl$_2$	NiCl$_2$
NaCl	🟧 ✓													
MgCl$_2$	🟧 ✓	🟩 ✓												
KCl	🟧 ✓	🟧 ✓	🟧 ✓											
RbCl	🟧 ✓													
CaCl$_2$	🟧 ✓	🟧 ✓	🟧 ✓	🟧 ✓										
CsCl	🟧 ✓	🟩 ✓	🟩 ✓											
PuCl$_3$		🟩 ✓	🟩 ✓											
UCl$_3$		🟩 ✓	🟩 ✓					🟩 ✓						
ZnCl$_2$		🟧 ✓	🟧 ✓	🟧 ✓		🟧 ✓								
MnCl$_2$		🟧 ✓	🟧 ✓	🟧 ✓		🟧 ✓				🟧 ✓				
FeCl$_2$		🟧 ✓	🟧 ✓	🟧 ✓		🟧 ✓				🟧 ✓	🟧 ✓			
CoCl$_2$		🟧 ✓	🟧 ✓	🟧 ✓		🟧 ✓				🟧 ✓	🟧 ✓	🟧 ✓		
NiCl$_2$		🟧 ✓	🟧 ✓	🟧 ✓		🟧 ✓				🟧 ✓	🟧 ✓	🟧 ✓	🟧 ✓	
SrCl$_2$	🟧 ✓	🟧 ✓	🟧 ✓	🟧 ✓		🟧 ✓								

🟩 ✓	In Model
🟧 ✓	In Literature

Figure 1. Matrix of fundamental pseudo-binary subsystems for the fluorides (left) and chlorides (right). The UF_3-UF_4 system is now assessed and therefore the matrix is updated to reflect the inclusion of those models in the MSTDB.

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[1] A thermodynamic assessment is a self-consistent set of Gibbs energy models for every phase in a particular system.

In molten salt fuel systems containing UF_4, the UF_4/UF_3 ratio is important for the control of the redox potential to, among other things, mitigate corrosion of structural materials. It is anticipated that a significant amount of both UF_4 and UF_3 will be continually present in the salt. An accurate and complete thermodynamic representation of the UF_4-UF_3 system is therefore critical to defining the chemistry of fluoride-based fuel.

A major contribution from this work is the assessment of the UF_3-UF_4 pseudo-binary. Using the CALPHAD method and FactSage thermodynamic software [2], a liquid solution representation was developed modified quasi-chemical (MQC) formalism, and a single solid solution, UF_{3+x}, which was modeled using a two sublattice polynomial model.

2. THERMODYNAMIC MODELING

2.1 CALCULATION OF PHASE DIAGRAM (CALPHAD) MODELS

The CALPHAD method [1] is the internationally recognized approach for development of thermodynamic representations of materials and is therefore recommended for MSR systems [3].

Pure elements and gas molecules along with stoichiometric compounds (both liquids and solids) are modeled as pressure independent phases with a temperature dependent polynomial given as:

$$G = a + b + cTlnT + dT^2 + eT^3 + fT^{-1} \dots$$

The general form of the molar Gibbs energy for solutions is given by the following equation:

$$G = G^{ref} - T\Delta S + G^{xs}$$

Here the first two terms represent an ideal mixing. G^{ref} is a weighted average of the Gibbs energies of each mixing constituent, the so called 'end members,' T is temperature, ΔS is the configurational entropy and G^{xs} modifies ideal behavior by taking into account interactions. The convention is to use a polynomial expansion in T and composition to represent G^{xs}, for example the Redlich Kister equation for binary solution given below.

$$G^{xs} = x_1 x_2\, {}^0L + x_1 x_2 \sum {}^iL(x_1 - x_2)^i$$

where x_i are molar fractions of component i and ${}^iL$ are termed interaction parameters.

The coefficients of G and G^{xs} are optimized using the largest reliable data set possible. This both improves confidence when interpolating within or extending beyond the limits of the experimental measurements and offers higher fidelity thermodynamic predictive capabilities.

As indicated in [3], the solution phase that needs the most attention for MSRs is the molten salt for which the modified quasichemical model (MQM) is used to represent.

The CALPHAD solution models can be extended to represent the highly multicomponent systems that will inevitably evolve in the molten salt fuel during operation. Further, they can be coupled to other physics via a solver, e.g. Thermochimica [4], to predict transport phenomena, nucleation, precipitation, corrosion and other material performance behavior [3].

2.2 SUB-SYSTEM ASSESSMENTS FROM THE LITERATURE

Systems with sufficient data available to perform a thermodynamic assessment are indicated by colored boxes in the matrices in Figure 1. Those in green were integrated into MSTDB and are available for computational applications.

2.3 THE UF_3-UF_4 SYSTEM

As the UF_3-UF_4 liquid behaves as an ideal solution of the two endmembers close to UF_4, the system has not yet been reported to be otherwise optimized. Experimental evidence, however, shows a deviation from ideality in the liquid, and the existence of an extensive UF_{3+x} solid solution. The current optimization has been performed in order to more accurately model the system beyond the dilute UF_3 region, which will help to increase the robustness of the molten salt thermodynamic database (MSTDB).

The UF_3-UF_4 assessment utilized the UF_3 and UF_4 thermodynamic values previously provided to MSTDB [5, 6]. This is required to maintain consistency within the MSTDB, with those values remaining the standard for use in thermodynamic modeling. The pure compound thermodynamic values are shown in Table 1. The definition of the Gibbs energy for pure compounds is given by the following equation:

$$G(T) = \Delta_f H^0(298.15) - S^0(298.15)T + \int_{298}^{T} C_p(T)dT - T\int_{298}^{T}\left(\frac{C_p(T)}{T}\right)dT$$

where $\Delta_f H^0$ (298.15) is the standard enthalpy of formation, S^0 (298.15) is the standard absolute entropy, and $C_p(T)$ is the temperature function of the heat capacity at constant pressure.

Table 1. Thermodynamic values of pure compounds used in the assessment.

Compound	$\Delta_f H^0(298.15)$	$S^0(298.15)$	$C_p = a + bT + cT^2 + dT^{-2}$		(J/mol*K)		Reference
	(kJ/mol)	(J/mol*K)	a	b T	c T^2	d T^{-2}	
UF_4 (cr)	-1914.200	151.70	114.519	2.06E-02	-	-4.13E+05	[1]
UF_4 (l)	-1914.658	115.40	174.74	-	-	-	[1]
UF_3 (cr)	-1501.400	129.22	106.541	7.05E-04	-	-1.04E+06	[2]
UF_3 (l)	-1500.897	103.66	130	-	-	-	[2]

The $UF_{(3+x)}$ solid solution was modeled using the two sublattice polynomial model. The first sublattice contains the cations (U^{3+} and U^{4+}), and the second sublattice contains the common anion (F^-). The endmembers use the Gibbs functions of the pure compounds from Table 1. The excess Gibbs energy is expanded as a polynomial shown below:

$$\Delta G^{xs} = \sum_{i\geq 1}\sum_{j\geq 1} Y_A^i Y_B^j L_{ij}$$

where Y_A and Y_B are the equivalent site fractions, and Lij are the optimized parameters.

The liquid solution was modeled using the modified quasi-chemical model in the quadruplet approximation. This is the selected model for the MSTDB salt liquids. The model contains two sublattices; the first contains the cations (A and B) and the second contains the common anion (F^-). For the second nearest neighbor pair formation reaction:

(A - F - A) + (B - F - B) = 2(A - F - B)

The Gibbs energy change of the second nearest neighbor pair formation is expanded as:

$$\Delta g_{AB/F} = \Delta g^0_{AB/F} + \sum_{(i+j)\geq 1} g^{ij}_{AB/F} \chi^i_{AB/F} \chi^j_{BA/F}$$

where $\Delta g^0_{AB/F}$ and $g^{ij}_{AB/F}$ are composition independent (end-member) functions which are optimized, and the $\chi_{AB/F}$ and $\chi_{BA/F}$ terms introduce the composition dependence of the Gibbs function. Charge neutrality is maintained and the cation-cation coordination numbers $Z^A_{AB/F}, Z^B_{AB/F}$, are used in representing short-range ordering (values for the cation-cation are shown in Table 2). The cation-cation coordination numbers for A = B are taken from the literature [5, 6]. The A ≠ B coordination numbers could be determined/optimized if necessary, but were left as their default values for this assessment.

Table 2. Cation-cation coordination numbers for the liquid solution.

A	B	$Z^A_{AB/F}$	$Z^B_{AB/F}$
U^{3+}	U^{3+}	6	6
U^{4+}	U^{4+}	6	6
U^{3+}	U^{4+}	6	6

2.3.1 Optimization of the UF_3-UF_4 system

Available experimental data for the UF_3-UF_4 system is extremely limited. The only experimental thermodynamic investigation of the system found was a 1974 publication from Thoma *et. al.* from ORNL [7]. The findings from this publication that were useful to this assessment include phase transition temperature and composition data as well as an estimated phase diagram(Table 3 and Table 1). There appears to be an error in the phase diagram from [7] as the UF_3 liquidus and solidus curves did not extend to the correct UF_3 melting point as stated in the publication (should be 1495°C not 1425°C). A corrected phase diagram is shown in Figure 2, where the red lines are the phase boundaries.

The liquid and solid solutions were optimized using the FactSage software based upon the data from Table 3 as well as transitions read from the corrected phase diagram (Figure 2). As no additional experimental data could be found regarding the boundary between UF3+x solid solution and UF4, the estimated dashed line of Figure 2 was taken as correct, however an increased error limit was applied.

Table 3. Phase transition data from [7].

UF3 mole %	Liquidus Temperature (°C)	Solidus Temperature (°c)
10	1006 ± 5	
		865 ± 4
15	975 ± 5	868 ± 5
20		868 ± 17
	951 ± 5	871 ± 8
25	921 ± 5	-
30	890 ± 5	876 ± 5
40	-	873 ± 5
43 ± 2	970 ± 5	
50		865 ± 4
68 ± 4		970 ± 5

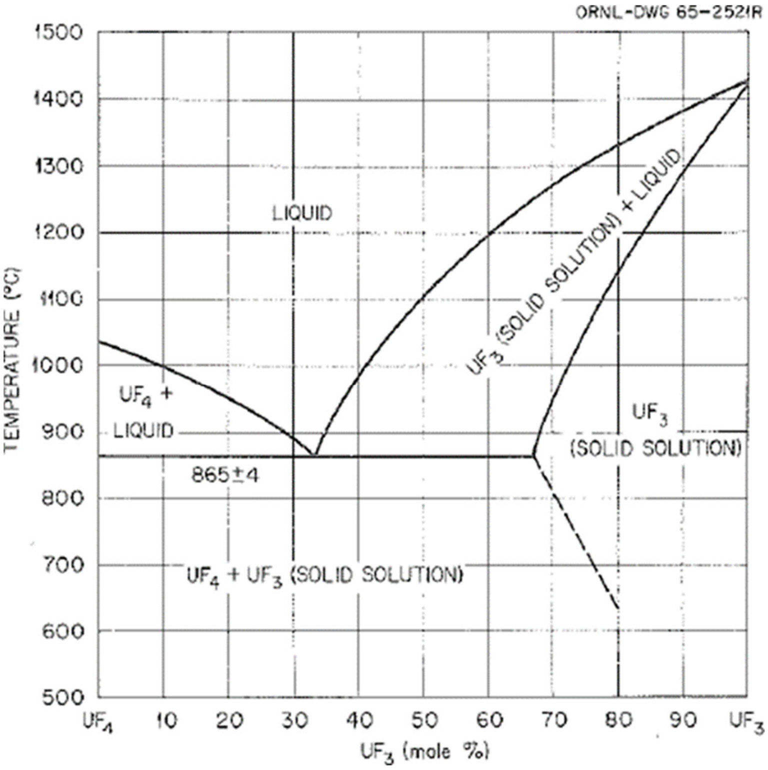


Figure 2. UF3-UF4 Phase diagram reported by Thoma et al [7].

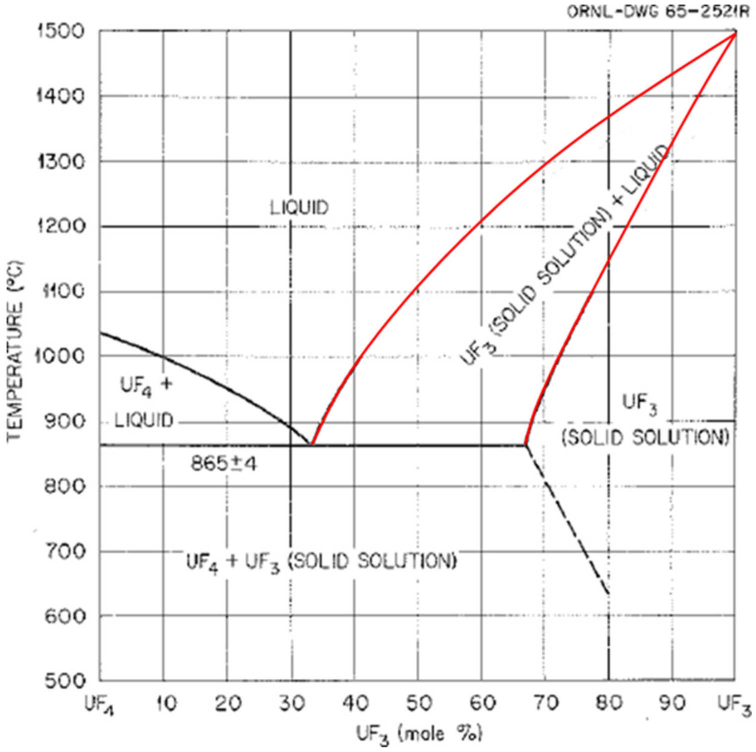


Figure 3. UF3-UF4 Phase diagram from [7] with UF3 melting point correction in red.

The excess Gibbs energy expression obtained from the optimization of the UF3+x solid solution is:

$$\Delta G^{xs} = (2186.03907 - 2.65690633 * T) * Y_{U4+} + 8427.09541 * Y_{U4+}^{3} + (3868.61246 - 1.95571113 * T) * Y_{U3+} * Y_{U4+}$$

The excess Gibbs energy term obtained from the optimization of the liquid solution is :

$$\Delta g_{U3U4/F} = -4501.82344 + 0.250861193 * T - 1003.69111 * \chi_{U3U4} * \chi_{U4U3}^{2}$$

The calculated UF_3-UF_4 phase diagram obtained from this assessment is shown in Figure 3. Good agreement is obtained between the calculated phase diagram and the available data. Only the boundary between UF_{3+x} and UF_4 shows notable deviation from the experimental diagram of Figure 2. As this boundary was only an estimation by Thoma *et al.[7]*, it will be assumed until new experimental data can be used to better define the it.

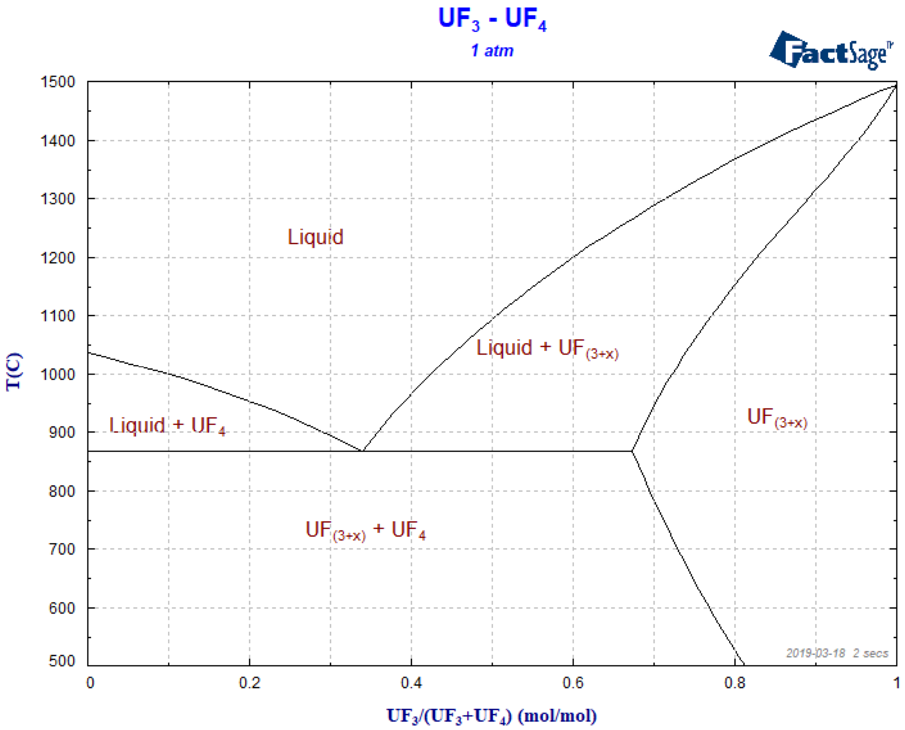


Figure 4. Calculated UF3-UF4 phase diagram from optimization.

The uncertainties obtained from the optimization for the excess Gibbs terms are shown in Table 4. The U3^n and U4^n columns refer to the exponent of the respective composition variable (Y or χ) in the excess Gibbs expansion. The T^n column refers to the exponent on temperature.

Table 4. Optimized values and uncertainties of excess Gibbs energy terms

Solution	U3^n	U4^n	T^n	Optimized Value	Uncertainty	Unit
Liquid	0	0	0	-4.502E+03	49	J
Liquid	0	0	1	2.509E-01	0.1	J
Liquid	1	2	0	-1.004E+03	50	J
Solid solution	0	1	0	2.186E+03	94	J
Solid solution	0	1	1	-2.657E+00	0.2	J
Solid solution	0	3	0	8.427E+03	329	J
Solid solution	1	1	0	3.869E+03	144	J
Solid solution	1	1	1	-1.956E+00	0.3	J

3. THE DATA PACKAGE

A data package documentation scheme was created in order to provide for self-consistent models developed from identified sources of data, and thus traceable for quality assurance purposes. The data package defines a single set of source values for elements and compounds utilized in the generation of relations for multicomponent stoichiometric compounds and solution phases for which they have yet to be determined. It is a roadmap, ensuring consistency among the multiple contributors to MSTDB, whether from first principles calculations or from existing or new measurements. The data package thus facilitates collaboration in the broader MSR thermodynamic community, helps define what new measurements or calculations are needed, and allows for tracking data to its source. The data package structure is outlined as follows:

1. Data extracted from literature
    a. For experimental or first principles computed values to be used in generating an assessment, provide a spreadsheet with values and units clearly indicated, and any error limits on values also provided. Sources for the values should be clearly indicated
    b. For thermodynamic values and/or solution parameters used directly in models, provide a spreadsheet again with any error limits. Sources for the values should be clearly indicated
2. Original experimental data
    a. Describe experimental procedures or reference to a document that contains those details (include document with data package).
    b. Provide original data in spreadsheet format (Appendix B) with values and units clearly indicated, and any error limits on values also provided.
3. Optimizations/assessments are performed and documented (each require their own spreadsheet)
    a. Sources and values for the endmember standard state data.
        i. Assure G functions for elemental values are consistent with those accepted/agreed upon for MSTDB.
        ii. Assure that endmember values for all systems are those accepted/agreed upon for MSTDB.
    b. Values and their sources for additional constituent/phase standard state data.
    c. For all phases provide description of the thermodynamic models used.
    d. Note any composition or temperature limits beyond which there is limited confidence in the results.
    e. Include computed phase diagrams and any property plots showing experimental/first principles computed points (from original work or literature) used in the assessments so as to allow comparison of data and values from assessed results. Show sources for each set of points.
    f. Text or reference to a document is required that describes how the optimization/assessment was performed.
4. Chemsage files
    a. Provide .dat file and use the following file naming convention that includes the composition and the current versions.
        i. Hyphens are used between the names of the components considered in the file. For example, Li-U-F when the elements are components, or LiF-UF4-BeF2 when the components are binary phases.
        ii. Provide a version number to delineate differences from earlier sets of values, for example “Ver 3.” So, an example would be “Li-U-F Ver 3.dat.” (Version enumeration will be decided by the person generating the datafile.)
    b. In first line of the .dat file, which is considered as solely text, provide a very brief description of the contents, your name and e-mail, and the date it was generated.

3.1 *MSTDB* CONTENT CONTROL AND AVAILABILITY

A critical element in maintaining a reliable and quality assured database is control over changes or additions to the contents. All new models and values must utilize the exact same standard state elemental and base compound values as all others within the database. Otherwise use of values for phases derived from differing standard state components will lead to inaccurate results. In addition, assessed systems not only need to be internally consistent, but are also required to generate the known phases/properties in computed interactions with additional components already accepted in the database. To safeguard the consistency and accuracy of the *MSTDB* it is necessary that there is a technical reviewer for each change to the database, with the responsibility to test the changes to be sure they meet the requirements for consistency and quality across the entire database. Thus, the mission is not only to provide for modifications and expansion of the database, but to assure its integrity through assuring consistency. This requires the *MSTDB's* technical reviewers to guard modifications to the database, allowing new versions with expanded content to be released only after quality assurance processes have been completed. Current planning is to move control of MSTDB from the initial developer at the University of South Carolina to ORNL with identification of appropriate staff and establishment of responsibilities.

The *MSTDB* is expected to be publicly available as it will be based on either generally available information or new models and values developed under federally funded programs. It is currently hosted on a password-protected website, code.ornl.gov, with access generally available from the ORNL website upon registration. Periodically the public *MSTDB* version will be updated as appropriate as new systems are added or revisions are required. As of this writing a decision has not been made as to whether MSTDB users will be allowed to modify the database for their own use, or whether it will be locked to any modifications. A non-public, unlocked version will be retained by the MSTDB development team and be available to MSR program participants who are generating new contributions and need to explore system behavior within the large context of the database.

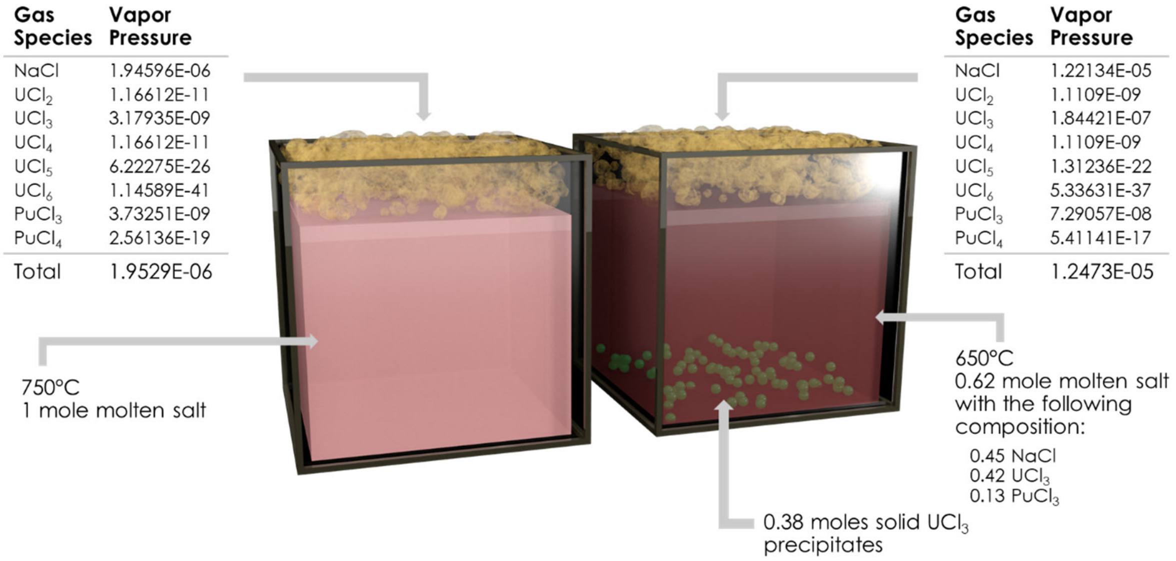
4. THERMODYNAMICS, THERMOPHYSICAL PROPERTIES, AND REACTOR MODELING

A molten salt fuel system will be continuously evolving due to transmutations, fission product generation, leaching of structural material constituents, unit operations like off gassing, precipitation of insoluble species, and other reactions. Because of the high temperatures, there is a rapid approach to equilibrium; therefore, thermodynamic arguments are fundamental for predicting these phenomena. As pointed out by McMurray and Besmann [8]:

> "…while thermodynamics does not explicitly include the physics of time evolution to equilibrium, the tendency of a system to evolve to its lowest energy state and to balance potentials does provide driving forces for many kinetic phenomena within certain formalisms, for example the theory of irreversible processes [9]. As mentioned, fuel experiences high temperatures. Thus, the assumption of local thermodynamic equilibrium (LTE) is useful for predicting the chemical state of the elements and the material properties of the fuel; these are important inputs for representing many kinetically driven processes like phase transformations, microstructural evolution and transport phenomenon."

4.1 THERMOPHYSICAL PROPERTIES

Within the MSR campaign, there is an effort to develop a thermophysical properties database to describe viscosity, thermal conductivity, volume expansion, and density. Thermophysical properties require a knowledge of the chemical state of the fuel system, e.g. equilibrium phases and compositions of those phases. This information must be provided by thermodynamics. A demonstration calculation of the chemical state of an example salt at two different temperatures using MSTDB is given in Figure 5.



Gas Species	Vapor Pressure
NaCl	1.94596E-06
UCl_2	1.16612E-11
UCl_3	3.17935E-09
UCl_4	1.16612E-11
UCl_5	6.22275E-26
UCl_6	1.14589E-41
$PuCl_3$	3.73251E-09
$PuCl_4$	2.56136E-19
Total	1.9529E-06

Gas Species	Vapor Pressure
NaCl	1.22134E-05
UCl_2	1.1109E-09
UCl_3	1.84421E-07
UCl_4	1.1109E-09
UCl_5	1.31236E-22
UCl_6	5.33631E-37
$PuCl_3$	7.29057E-08
$PuCl_4$	5.41141E-17
Total	1.2473E-05

Figure 5. Chemical state calculation results using MSTDB with FactSage thermodynamic software for an example salt consisting of 0.28 NaCl, 0.64 UCl3, and 0.08 PuCl3 by mole.

4.2 MASS ACCOUNTANCY

Mass accountancy within the MSR campaign is currently focused upon the following phenomena:

- Vapor phase transport for tracking of volatile radionuclides (Cs, I, Xe, etc.) that can leave through exhaust gas processing
- Tritium transport via diffusion mechanism
- Species dissolution from structural materials into the molten salt
- Precipitation and deposition of fission and corrosion products from the salt onto containment surfaces

Thermodynamics defines what reactions can occur and provides driving forces, such as chemical potentials and vapor pressures for modeling mass transport. The MSTDB will be coupled to multi-physics codes via the Thermochimica equilibrium solver to describe these behaviors for MSR mass accountancy.

4.3 THERMOCHIMICA

Thermochimica is an open source stand-alone thermodynamics solver that has been designed for direct integration into multi-physics codes. Conventional computational thermodynamic software packages are proprietary and cannot be used for multi-physics simulations such as those under development by DOE programs aimed at simulating reactor performance. Therefore, development of Thermochimica to be compatible with new tools and associated models is an ongoing activity within DOE NE.

4.4 EXPERIMENTS

Experimental thermochemistry provides fundamental inputs for optimizing adjustable model parameters in order to assess the systems of interests. Information of interest includes phase equilibria data, heat capacities, enthalpies of transition, vapor pressures, and species activities. The MSR campaign collaborates across many national labs that together maintain a suite of thermal analysis instrumentation and capabilities including X-ray and neutron diffraction, calorimetry, electrochemistry, and evolved gas analysis (EGA). In FY18 a Netzsch STA 409 CD 403/5/G STA-MS Skimmer Coupling System was purchased. This instrument performs simultaneous thermal analysis (STA)[2] and enables EGA of materials up to 2000°C (1450°C in oxidizing environments). with a shortened, heated transfer route to a quadrupole mass spectrometer (QMS) to mitigate or eliminate species condensation and allow detection by the QMS.

The Netzsch STA 409 CD 403/5/G STA-MS Skimmer Coupling System was delivered to Oak Ridge National Laboratory in early April 2019 and installed in May 2019. The instrument was verified to be functional by performing thermal analysis on a non-hazardous, well characterized standard. That standard was calcium salt of oxalate and it behaved as expected. Thermo-gravimetric analysis showed predictable weight loss and evolved gas species for the decomposition reactions at temperatures previously established by similar and/or other methods. Further, the melting/freezing temperature for Au was verified using the Skimmer in differential scanning calorimetry (DSC) mode. Since, measurements have been performed to determine vapor species over $MgCl_2$ with varying degrees of hydration to aid in understanding the impact of impurities (i.e. H_2O) on the corrosion mechanism of $MgCl_2$ containing salts with structural materials that use Cr as an alloying component.

5. SUMMARY AND CONCLUSION

The first version of the MSTDB was developed using the CALPHAD approach. It currently includes 21 elements with models for 54 molten salt binary solutions, 26 ternary molten salt solutions, 14 solid solutions, and 140 multicomponent, stoichiometric compounds.

It is expected that the MSTDB will continue to be developed with respect to additional elements, and the construction of higher order systems that are needed to represent practical MSR salt compositions. Prioritization will allow the addition of constituents and expansion of systems that are considered to be most important to development of the diverse MSR concepts and the needs of regulators. This will eventually include all the elements that will exist during operation of a molten salt reactor to model the thermochemical behavior with burnup including additives and corrosion products. Key to quality assurance and maintaining internal consistency of MSTDB is the data package. The data package thus facilitates collaboration in the broader MSR thermodynamic community and defines what new measurements or calculations are needed. In addition, means for quality assurance of the MSTDB have been outlined.

An optimization of the UF_3-UF_4 system was needed and performed. The excess Gibbs parameters were obtained which provide good agreement with the available experimental data. Additional experimental effort is recommended in order to better define the phase boundary between UF_{3+x} solid solution and UF_4.

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[2] Simultaneous thermal analysis is the use of thermogravimetry coupled with MS and/or calorimetry.

ACKNOWLEDGEMENTS

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APPENDIX A. MSTDB SOLUITON AND COMPOUND LIST

APPENDIX A. MSTDB SOLUTION AND COMPOUND LIST

MSTDB Solution and Compound Lists 05-02-2019

Pseudo-Binary Solutions

54 total

- NaF-LiF
- BeF2-LiF
- KF-LiF
- RbF-LiF
- CaF2-LiF
- ThF4-LiF
- PuF3-LiF
- UF4-LiF
- UF3-LiF
- CsF-LiF
- CeF3-LiF
- LaF3-LiF
- BeF2-NaF
- KF-NaF
- RbF-NaF
- CaF2-NaF
- ThF4-NaF
- PuF3-NaF
- UF4-NaF
- UF3-NaF
- CsF-NaF
- LaF3-NaF
- ThF4-BeF2
- PuF3-BeF2
- UF4-BeF2
- RbF-KF
- CaF2-KF
- PuF3-KF
- CsF-KF
- LaF3-KF
- PuF3-RbF
- CsF-RbF
- LaF3-RbF
- ThF4-CaF2
- LaF3-CaF2
- PuF3-ThF4
- UF4-ThF4
- CsF-ThF4
- CeF3-ThF4
- UF4-PuF3

- CsF-PuF3
- LaF3-PuF3
- RbF-UF4
- CaF2-UF4
- LaF3-CsF
- NaCl-MgCl2
- NaCl-CsCl
- NaCl-PuCl3
- NaCl-UCl3
- MgCl2-CsCl
- MgCl2-PuCl3
- MgCl2-UCl3
- MgCl2-KCl
- PuCl3-UCl3

Pseudo-Ternary Solutions
26 total

- $LiF-BeF_2-UF_4$
- $LiF-BeF_2-ThF_4$
- $LiF-BeF_2-NaF$
- $LiF-BeF_2-PuF_3$
- $LiF-NaF-UF_4$
- $LiF-ThF_4-PuF_3$
- $LiF-CaF_2-ThF_4$
- $LiF-UF_4-PuF_3$
- $LiF-LaF_3-CsF$
- $LiF-NaF-LaF_3$
- LiF-NaF-RbF
- $LiF-NaF-PuF_3$
- $LiF-CsF-PuF_3$
- $NaF-BeF_2-ThF_4$
- $NaF-BeF_2-UF_4$
- $NaF-BeF_2-PuF_3$
- $NaF-UF_4-ThF_4$
- $NaF-KF-CaF_2$
- LiF-KF-NaF
- LiF-KF-CsF
- LiF-KF-RbF
- $LiF-KF-CaF_2$
- $LiF-CaF_2-LaF_3$
- $LiF-CeF_3-ThF_4$
- $NaF-CaF_2-LaF_3$
- $BeF_2-UF_4-ThF_4$

Solid Solutions

14 total

- (La, Pu)F_x
- (Li, Na)$_7$Th$_6$F$_{31}$
- (Th, U, Pu)F_x
- Li(Th, U)$_4$F$_{17}$
- Li(Th, U)$_2$F$_9$
- Li$_7$(Th, U)$_6$F$_{31}$
- Li$_3$(Th, U)F$_7$
- Na$_2$(Th, U)F$_6$
- Na$_7$(Th, U)$_6$F$_{31}$
- Na(Th, U)$_2$F$_9$
- (Ca, La)F_x
- (Ca, Th)F_x
- (Li, Na, K, Rb, Cs)F
- (Ce, Th)F_x

Pure Compounds

140 total

- Be
- BeF2
- Ca
- CaF2
- CaThF6
- Ce
- CeF3
- CeTh2F11
- CeThF7
- Cl
- Cl2
- Cr
- CrCl2
- CrCl3
- CrCl4
- CrCl5
- CrCl6
- Cs
- Cs2MgCl4
- Cs2Th3F14
- Cs2ThF5
- Cs2ThF6
- Cs3LaF6
- Cs3MgCl5
- Cs3PuF6

- Cs3ThF7
- CsCaCl3
- CsCl
- CsF
- CsMg3Cl7
- CsMgCl3
- CsTh2F9
- CsTh3F13
- CsTh6F25
- F
- F2
- K
- K2
- K2F2
- K2MgCl4
- K2MgF4
- K2NiF4
- K3LaF6
- K3Mg2Cl7
- K3PuF6
- KCaF3
- KCl
- (KCl)2
- KF
- KLaF4
- KMgCl3
- KMgF3
- KNiF3
- KPuF4
- La
- LaF3
- Li
- Li2BeF4
- Li2CaThF8
- Li2NiF4
- LiBeF3
- LiCs2Cl3
- LiCsF2
- LiF
- LiNa2Be2F7
- LiNa5Be3F12
- LiNaBeF4
- LiRbF2
- Mg
- Mg2
- MgCl
- MgCl2
- Na

- Na2BeF4
- Na2MgCl4
- Na2ThF6
- Na2UF6
- Na3BeTh10F45
- Na3Th2F11
- Na3UF7
- Na4ThF8
- Na5U3F17
- Na7Th2F15
- Na7Th6F31
- Na7U6F31
- NaBeF3
- NaCeF4
- NaCl
- NaF
- NaLaF4
- NaMgCl3
- NaNiF3
- NaPuF4
- NaTh2F9
- NaThF5
- NaU2F9
- NaU4F17
- NaUF4
- Nd
- Ni
- NiF2
- Pu
- PuCl3
- PuCl4
- PuF
- PuF2
- PuF3
- PuF4
- PuF6
- Rb
- Rb2LaF5
- Rb2PuF5
- Rb3LaF6
- Rb3PuF6
- RbF
- RbLa2F4
- RbLaF4
- RbPuF4
- Sr
- Th
- Th2F9Li

- Th2PuF11
- Th4F17Li
- ThF4
- ThF5Li
- ThF7Li3
- U
- U2PuF11
- U4F17Li
- U6F31Li7
- UCl2
- UCl3
- UCl4
- UCl5
- UCl6
- UF3
- UF4
- UF8Li4
- Zn
- Zr

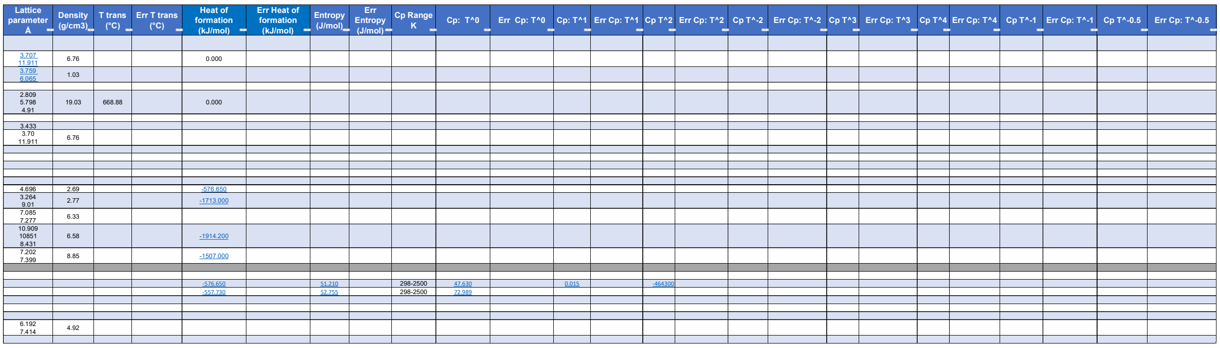
APPENDIX B. THERMODYNAMIC ASSESSMENT DATA PACKAGE TEMPLATE

APPENDIX B. THERMODYNAMIC ASSESSMENT DATA PACKAGE TEMPLATE

Table A.1. Checklist.

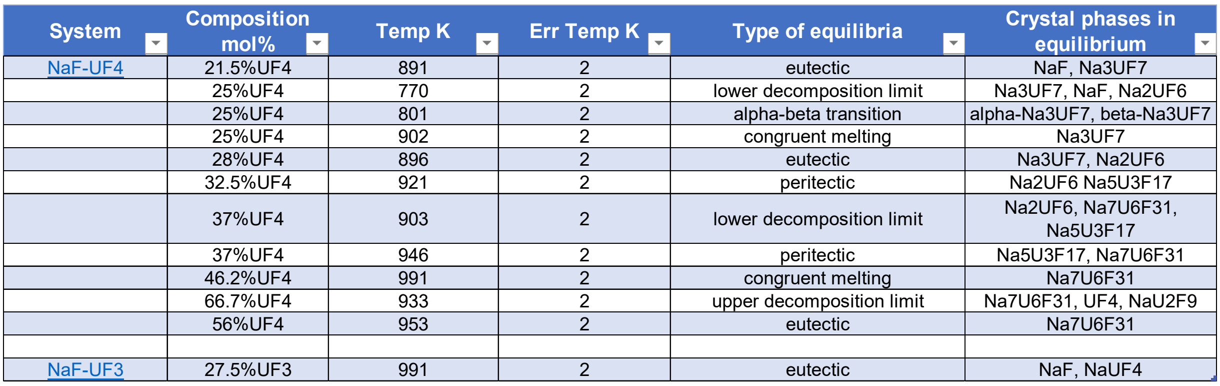
Data Package Checklist for the System: *name of system and version*	✓
	☐
Extracted Data	☐
Property values in spreadsheet with error limits	☐
Sources	☐
Derived thermodynamic values with error limits	☐
Sources	☐
Original Experimental Data	☐
Values spreadsheet with error limits	☐
Experimental procedures text or reference provided	☐
Optimizations/Assessment	☐
Spreadsheet with accepted elemental and endmember G functions used and sources	☐
Spreadsheet with used literature thermo values for other constituents and sources	☐
Spreadsheet of all optimization property data used, error limits, and sources	☐
Description of thermodynamic models for used for each of the phases	☐
Temperature and composition limits for use of assessed values	☐
Computed phase diagram and property plots showing data points used and sources	☐
Text or reference as to details of how optimization/assessment was performed	☐
Generation of .dat files	☐
Naming convention followed – System and version	☐
Description provided in first line of file	☐

Table A.2. Example compound data.



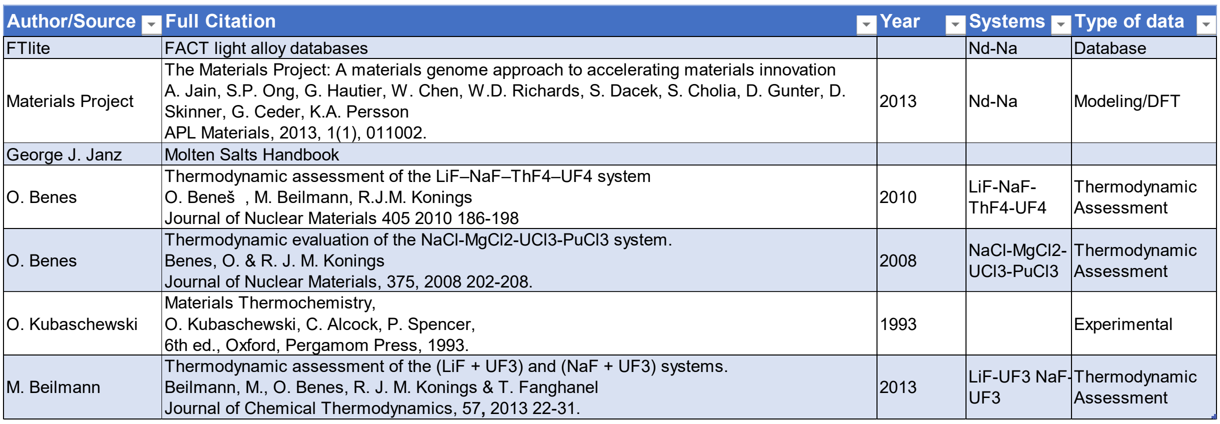
Lattice parameter Å	Density (g/cm3)	T trans (°C)	Err T trans (°C)	Heat of formation (kJ/mol)	Err Heat of formation (kJ/mol)	Entropy (J/mol)	Err Entropy (J/mol)	Cp Range K	Cp: T^0	Err Cp: T^0	Cp: T^1	Err Cp: T^1	Cp T^2	Err Cp: T^2	Cp T^-2	Err Cp: T^-2	Cp T^3	Err Cp: T^3	Cp T^4	Err Cp: T^4	Cp T^-1	Err Cp: T^-1	Cp T^-0.5	Err Cp: T^-0.5
3.707 11.911	6.76			0.000																				
3.759 6.065	1.03																							
2.809 5.798 4.91	19.03	668.88		0.000																				
3.433																								
3.70 11.911	6.76																							
4.696	2.69			-576.650																				
3.264 9.01	2.77			-1713.000																				
7.085 7.277	6.33																							
10.909 10851 8.431	6.58			-1914.200																				
7.202 7.399	8.85			-1507.000																				
				-576.650		51.210		298-2500	47.630		0.015		-464300											
				-557.730		52.755		298-2500	72.989															
6.192 7.414	4.92																							

Table A.3. Example phase diagram data for U-Na-F system.



System	Composition mol%	Temp K	Err Temp K	Type of equilibria	Crystal phases in equilibrium
NaF-UF4	21.5%UF4	891	2	eutectic	NaF, Na3UF7
	25%UF4	770	2	lower decomposition limit	Na3UF7, NaF, Na2UF6
	25%UF4	801	2	alpha-beta transition	alpha-Na3UF7, beta-Na3UF7
	25%UF4	902	2	congruent melting	Na3UF7
	28%UF4	896	2	eutectic	Na3UF7, Na2UF6
	32.5%UF4	921	2	peritectic	Na2UF6 Na5U3F17
	37%UF4	903	2	lower decomposition limit	Na2UF6, Na7U6F31, Na5U3F17
	37%UF4	946	2	peritectic	Na5U3F17, Na7U6F31
	46.2%UF4	991	2	congruent melting	Na7U6F31
	66.7%UF4	933	2	upper decomposition limit	Na7U6F31, UF4, NaU2F9
	56%UF4	953	2	eutectic	Na7U6F31
NaF-UF3	27.5%UF3	991	2	eutectic	NaF, NaUF4

Table A.4. Example of reference log for several systems important for the MSTDB development.



Author/Source	Full Citation	Year	Systems	Type of data
FTlite	FACT light alloy databases		Nd-Na	Database
Materials Project	The Materials Project: A materials genome approach to accelerating materials innovation A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson APL Materials, 2013, 1(1), 011002.	2013	Nd-Na	Modeling/DFT
George J. Janz	Molten Salts Handbook			
O. Benes	Thermodynamic assessment of the LiF–NaF–ThF4–UF4 system O. Beneš , M. Beilmann, R.J.M. Konings Journal of Nuclear Materials 405 2010 186-198	2010	LiF-NaF-ThF4-UF4	Thermodynamic Assessment
O. Benes	Thermodynamic evaluation of the NaCl-MgCl2-UCl3-PuCl3 system. Benes, O. & R. J. M. Konings Journal of Nuclear Materials, 375, 2008 202-208.	2008	NaCl-MgCl2-UCl3-PuCl3	Thermodynamic Assessment
O. Kubaschewski	Materials Thermochemistry, O. Kubaschewski, C. Alcock, P. Spencer, 6th ed., Oxford, Pergamom Press, 1993.	1993		Experimental
M. Beilmann	Thermodynamic assessment of the (LiF + UF3) and (NaF + UF3) systems. Beilmann, M., O. Benes, R. J. M. Konings & T. Fanghanel Journal of Chemical Thermodynamics, 57, 2013 22-31.	2013	LiF-UF3 NaF-UF3	Thermodynamic Assessment