



Fundamental Issues Identified for Thermodynamic Description of Molten Salt Systems

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Abstract Thermodynamic modeling of the molten salt systems is critical in the design of advanced nuclear power plants, materials recycling, and many other important clean energy applications. As one of the most capable computational thermodynamic approaches, the CALPHAD (Calculation of Phase Diagrams) method has been widely used for multicomponent thermodynamic database development and further support more physics-based modeling. Although considerable CALPHAD modeling efforts for molten salt systems have been made, we found that no evaluation has been performed regarding the unary thermodynamic models for the molten salt systems despite the fact that more than one pure substance database is available for the CALPHAD modeling. Therefore, the thermodynamic descriptions of the pure salts should be critically evaluated to ensure a high-fidelity molten salt thermodynamic database. In this work, we comprehensively analyzed some selected molten salts using different available thermodynamic descriptions from two databases as an example. One is the SSUB database released by the SGTE (Scientific Group Thermodata Europe), and the other is the FactPS database from the FactSage. The significant

discrepancies observed in the thermodynamic description between the existing CALPHAD pure substance databases and experiments call for an urgent effort to improve.

Keywords molten salt · nuclear · pyroprocessing · recycle · sustainability · thermodynamics

1 Introduction

The CALPHAD (Calculation of Phase Diagrams) approach is a powerful materials genome tool^[1–4] to predict phase diagrams, phase equilibria, and phase transformations, which are critical for materials design and processing optimization. Although the CALPHAD methodology has been developed for several decades with many commercial software and databases available, the potential of applications can be extended further if the database and thermodynamic models describing materials thermodynamics are highly accurate. Thanks to the creation of the SGTE (Scientific Group Thermodata Europe) pure element database in 1991, under the efforts of a group of CALPHAD pioneers,^[5] all multicomponent databases had a common ground for the development and integration of different versions of databases. Such a concept can be understood naturally as a tree structure shown in Fig. 1.

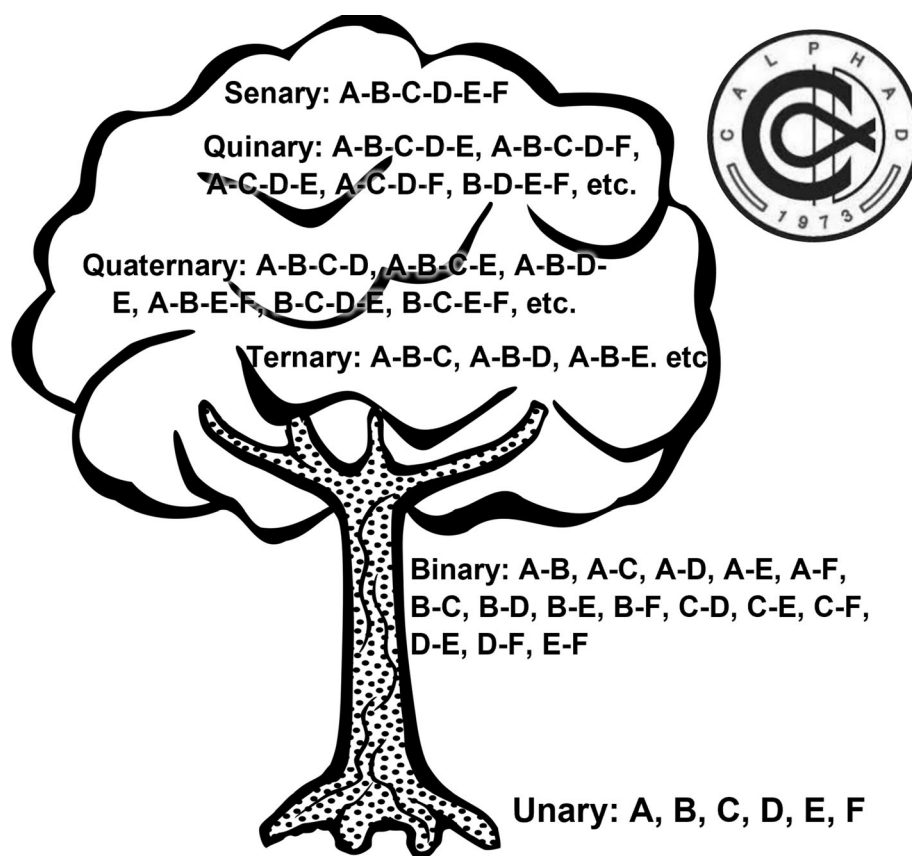
Because of such a pure substance, i.e., unary database, multicomponent CALPHAD database development becomes more effective. It directly resulted in the flourishing of CALPHAD databases for metals and alloys. Nowadays, almost every CALPHAD software company develops commercial thermodynamic and diffusion databases, which are essential for materials and processing design. For example, one needs to consider alloying effects

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Fig. 1 CALPHAD tree indicates the relationships between unary, binary, ternary, and higher-order systems for database development



to enhance the strength and ductility during steel development, and commercial CALPHAD steel databases are now readily available. These databases are usually sold together with the software, such as TCFE databases from Thermo-Calc,^[6] PanIron from CompuTherm,^[7] or FSsteel from FactSage.^[8] It is noteworthy that many of these metal and alloy databases have been developed over several decades.

Despite the common agreement on the pure element database, one should realize that developing a comprehensive CALPHAD database covering multicomponent and multiphase with high fidelity is a challenging task, although some automation methods and software packages, including artificial intelligence techniques, indicate a promising future for CALPHAD database development.^[9] In addition, many efforts have been made for non-metallic systems, such as oxides. Although the CALPHAD software companies also release oxide databases, the number of the database for oxide systems is smaller than for metals and alloys. In fact, modeling the oxide systems can be much more challenging by considering the complexity resulting from the requirement of charge balance, which is not required as an extra equilibrium constraint for alloy systems.

Recently we have noticed another serious issue for the molten salt database development, which can have significant impact on the application of CALPHAD in molten salt engineering. Similar to or even worse than for oxide systems, the development of molten salt databases is rather limited in comparison to alloy databases. In this work, we will examine several key molten salts such as KCl, LaCl₃, LiCl, NaCl, and UCl₃ as examples to elucidate the issues identified in thermodynamic description of the unary molten salts.

2 Thermodynamic Description of the Unary Systems

As indicated in Fig. 1, during the CALPHAD database development, the most critical step in the beginning is the thermodynamic modeling of the unaries. In fact, the CALPHAD community has realized this importance which resulted in the 1991 release the pure element database for the Gibbs energies in their stable structure and differences among different structures (i.e., phases), which is also called as lattice stability.^[5]

As shown in Fig. 1, if someone has to perform an assessment of the A-B-C-D-E system, in which, A, B, C, D,

and E, are unaries, the higher order systems require to use the same thermodynamic function of the lower order systems to ensure the model compatibility. Therefore, if thermodynamic description of one unary lacks accuracy, the “snowball effect” will lead to the degradation of the quality of the entire multicomponent database. In addition, if one of the lower order systems requires modification, all the related higher order systems need adjustment accordingly.

It should be mentioned that, although the thermodynamic modeling of molten salt systems has been performed for many years resulting in numerous publications, most of the databases are developed using the two substance databases. One is SSUB, the SGTE (Scientific Group Thermodata Europe) substance database,^[10] and the other is the FactPS database,^[8] the pure substance thermodynamics released by FactSage.^[8] Therefore, it is essential to understand the accuracy of the unary database better. Although only these two databases will be discussed in the present work more databases with thermodynamic descriptions of substances are available, such as the HSC^[11] or MALT^[12] databases are available.

3 Case Studies of Selected Molten Salts

In this work, case studies will be performed for the following unary systems: KCl, LaCl₃, LiCl, NaCl, and UCl₃ as basis for a thermodynamic database of the multicomponent salts, which is under development at the University of Pittsburgh for molten salt reactor applications. Both unary databases, SSUB (version 6) and FactPS, are considered for such a comparison evaluating the accuracy of thermodynamic descriptions. The original experimental data reported in the literature are used to benchmark the thermodynamic quantities. If the original experimental data are not available, the handbook evaluation of the thermodynamic properties will be considered as a reference. However, the latter cannot be a replacement of the reported experiments since many of the evaluations include estimated extrapolations from the ranges with experimental data. The comparison will be made mainly for the heat capacity, and its derived thermodynamic properties, such as, enthalpy, entropy, and Gibbs energy. Due to a lack of experimental data, thermodynamic description for the liquid phase of UCl₃ is not available in the SSUB database. As a result, thermodynamic properties predicted by SSUB are merely presented for solid UCl₃. Therefore, more efforts in both experiments and modeling should be made to improve the available thermodynamic modeling.

3.1 Comparison of Heat Capacity

The most critical physical quantity in the CALPHAD approach is the heat capacity, which is assessed based on the experimental specific heat data. However, for nonstable regions such as some ultra-high and ultra-low temperature ranges or the nonstable phases, theoretical extrapolated values or quantum mechanical calculations can help to provide some reasonable data, although it can be difficult to quantify the uncertainty in many cases. Therefore, the primary resources for thermodynamic description of unary systems are the experimental data reported in the open literature.

As shown in Fig. 2, the calculated heat capacity of the pure salts by using the FactPS database are fairly poor, despite the fact that this thermodynamic database has been widely used in building many multicomponent databases including some commercial databases by FactSage. Meanwhile, although it is hard to achieve a satisfactory comparison between experimental data and model-prediction, the discrepancy is significantly less for the SSUB database. In this work, the heat capacity and other thermodynamic properties below 298.15 K are plotted to compare with experimental information. However, one should be aware that that the second-generation thermodynamic models for unary database are not capable to capture the physics for such a low temperature range. Nevertheless, we hope that the collected experimental dataset at low temperature will be valuable for the future unary database development.

No experimental data are available for the heat capacity of the liquid phase of the selected pure salts, except for the evaluated values from handbooks, such as JANAF^[13] and Barin.^[14] Above the melting point, the heat capacity of the liquid phase computed by CALPHAD databases agrees well with the evaluation in the handbooks, except for LaCl₃. For the heat capacity of LaCl₃, the FactPS database predicts a much lower value compared to the handbook value, while it agrees well with the prediction by the SSUB database. Below the melting point, the calculated heat capacity of the solid phase using the SSUB databases agrees well with the experiments above 273.15 K. Comparing the heat capacity for NaCl, which is a common salt in many applications, the agreement between FactPS modeling and experiments is unsatisfactory from 800 K to the melting point. In fact, a close look at the case of another common salt, KCl, the thermodynamic model provided by the FactPS database also fails to accurately predict the heat capacity about 100 K below the melting point. However, the comparison of heat capacity for both NaCl and KCl between calculation using the SSUB database and experiments are satisfactory.

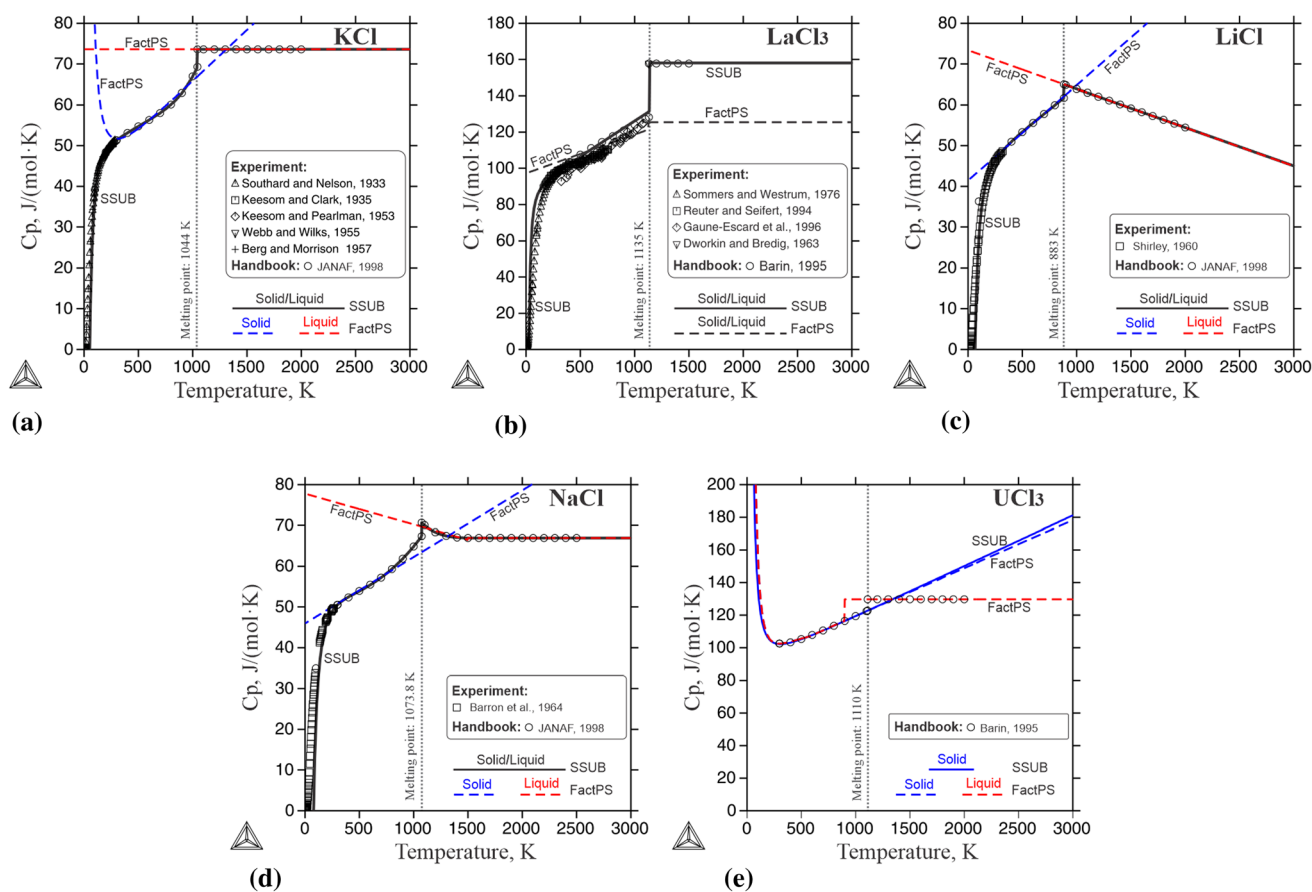


Fig. 2 Comparison of heat capacity between CALPHAD model-prediction and experimental information of pure salts: (a) KCl^[15–19], (b) LaCl₃^[14,20–24], (c) LiCl^[13,25], (d) NaCl^[13,26], and (e) UCl₃^[14].

It is noteworthy that the thermodynamic description regarding the choice of breakpoints on C_p curve in the FactSage are not always matching the phase transition temperature. According to the FactPS database, the heat capacity for LaCl₃ is discontinuous at 1128 K, which is 8 K lower than the melting point. As shown in Fig. 2(e), an obvious discontinuity at 900 K can be observed from the C_p curve of liquid UCl₃. The reason of choosing a different value from the phase transition temperature is unclear.

3.2 Comparison of Enthalpy and Entropy

The advantage of the CALPHAD method is not merely for the phases in their own stable temperature ranges. More importantly, CALPHAD computations based on a high-quality database can predict the nonstable range,^[27,28] in which experiments are difficult to perform. A comparison on the heat content and entropy as a function of temperature as shown in Figs. 3 and 4 may be able to address this and further evaluate the quality of these two databases.

Since both enthalpy and entropy are directly related to heat capacity, it is not surprising to observe a similar level

Note that when the experimental measurement is not available, estimated values from Handbooks^[13,14] are considered

of agreement in the comparison of these quantities. Furthermore, due to the fact that these quantities are an integral of heat capacity, the difference is much more pronounced and can provide a better guideline for the future modeling efforts for improvement.

Figure 3 presents the comparison of heat content between thermodynamic descriptions from CALPHAD databases and experimental information. Similar to the heat capacity, the comparison of heat content also indicates a better thermodynamic description of these selected molten salts in the SSUB than the FactPS database. Moreover, another strong concern related to the FactPS database is the extrapolated phase stability. Except for the LaCl₃ salt, the thermodynamic description of the FactPS database will introduce a higher heat content of solid than that of liquid at a certain high temperature above the melting point. Apparently, this is unphysical. In addition to this, the comparison of entropy of LiCl shown in Fig. 4(c) also demonstrates that the predicted entropy of the solid phase will be higher than the liquid phase at temperatures above 2626 K, which will cause unphysical stabilization of the solid phase.

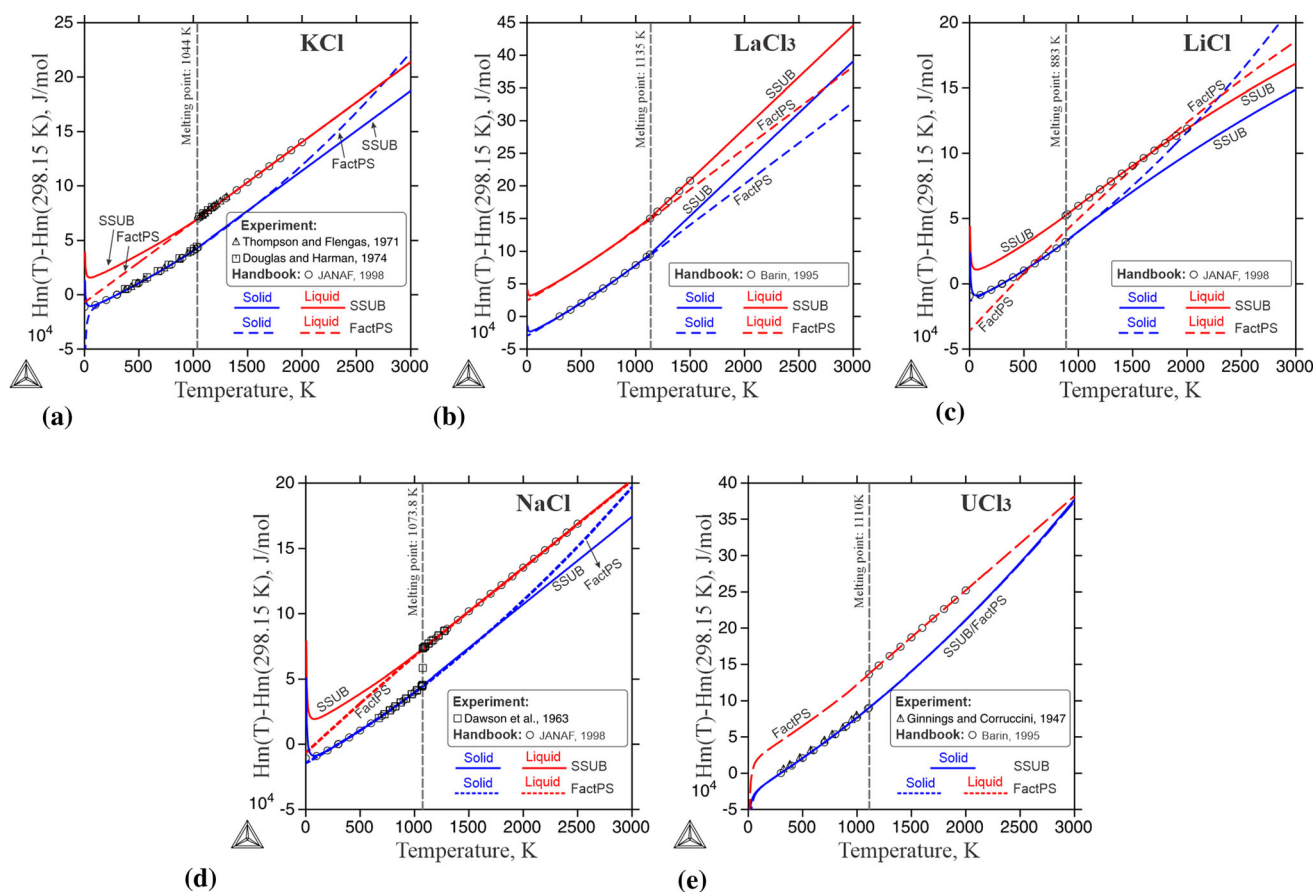


Fig. 3 Comparison of heat content between CALPHAD model-prediction and experimental information of pure salts: (a) KCl^[13,29,30], (b) LaCl₃^[14], (c) LiCl^[13], (d) NaCl^[13,31], and

(e) UCl₃^[14,32]. Note that when the experimental measurement is not available, estimated values from Handbooks^[13,14] are considered

3.3 Comparison of Gibbs Energy

Similar to the entropy terms, although the Gibbs energies cannot be measured directly, the modeling accuracy of heat capacity determines the reliability of the Gibbs energy functions. In fact, when comparing the Gibbs free energy curves between these two databases, some of the issues related to the identified low-fidelity model-predictions become clearer. Figure 5 shows the relative Gibbs energy using the solid phase as the reference state over the temperature between 298.15 and 6000 K. Obviously, for both KCl and LiCl the solid state phase is stable again at high temperature. Although it is hard to estimate what caused such an unsatisfactory thermodynamic description, such a nonphysical feature in the FactPS database is rather easy to fix. Furthermore, the strange curvature of the Gibbs energy developed at both high and low temperature for salts KCl, LiCl, NaCl, and UCl₃ using the FactPS description is rather unnecessary.

4 Suggestions on Improving Thermodynamic Modeling of Molten Salts

The observed imperfections of the existing salt unary databases are surprisingly severe and should be fixed by the CALPHAD and salt communities rather sooner than later. According to the CALPHAD tree discussed in Fig. 1, such a discrepancy between thermodynamic modeling and experimental data for pure salts will further propagate and cause unsolvable issues for multicomponent databases. It should be highlighted that although molten salt is currently increasingly of interest to the nuclear community, databases developed for this purpose can be shared with other research communities. In addition, due to lack of databases, the current focus of the CALPHAD modeling application in the nuclear molten salt community is more about phase diagram computation rather than prediction of metastable phase stability or even thermodynamic properties. The great potential of the CALPHAD approach in predicting nonequilibrium with nonstable phase behavior is often not fully comprehended during the initial stages of applying the CALPHAD method. Therefore, more efforts

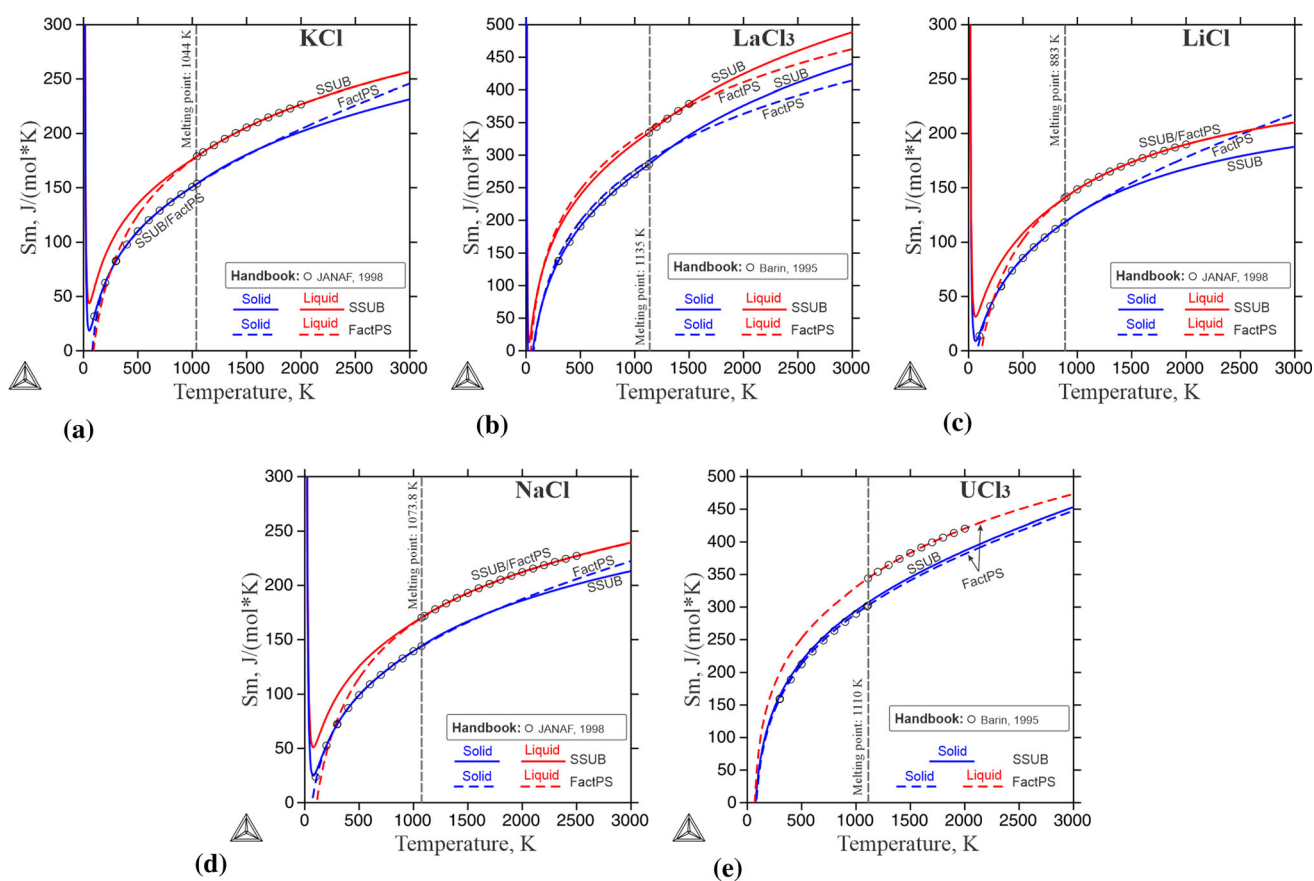


Fig. 4 Comparison of entropy between CALPHAD model-prediction and estimated values by Handbooks^[13,14] of pure salts: (a) KCl, (b) LaCl₃, (c) LiCl, (d) NaCl, and (e) UCl₃

are required to make such a change in the molten salt application field, where the CALPHAD approach is still a relatively new tool. Comparing with the alloy and oxide databases, the molten salt databases are still in the beginning stage of development, and thus allow more constructive efforts such as modeling of the unary substances. One should also realize that potential applications of the molten salt databases will be extended significantly not only for nuclear reactors, but also for other energy applications, such as battery recycling. These applications often require a good understanding of the thermodynamics and particularly phase stability and phase transformations. Therefore, they can stimulate the CALPHAD model and database development for the multicomponent molten salt systems. However, an accurate unary database is crucial as the basis for such potential applications.

Although there may be more ongoing efforts of multicomponent molten salt database development based on the SSUB and FactPS databases, it is important to realize the issues described in the present work may result in more inconsistencies between model-predictions and experiments. One should keep in mind that the reassessment of the thermodynamic parameters for an unary molten salt is

often much less complicated than the reassessment of binary and higher order systems. However, one should invest more time in data acquisition of experimental data, such as heat capacity, enthalpy of mixing, activity, etc., for the assessment. Especially, for salts lacking experiments, one may find valuable information for the unary from experimental work of binary and higher-order systems, and thus can obtain reasonable value based on extrapolation.

The wide application of the CALPHAD approach would not have been possible without the public release of the SGTE pure element database.^[5] Therefore, an openly accessible unary salt database similar to the pure element by the SGTE will promote more molten salt database development. Meanwhile, during the CALPHAD application based on the existing unary databases, one should be aware of their limitations including the issues identified in this work.

Indeed, for a while there may be contradictory thermodynamic descriptions during the CALPHAD database development of the molten salt systems. On the one hand, a good unary database still requires significant efforts in both CALPHAD and molten salt communities. On the other hand, some of the immediate use of the CALPHAD

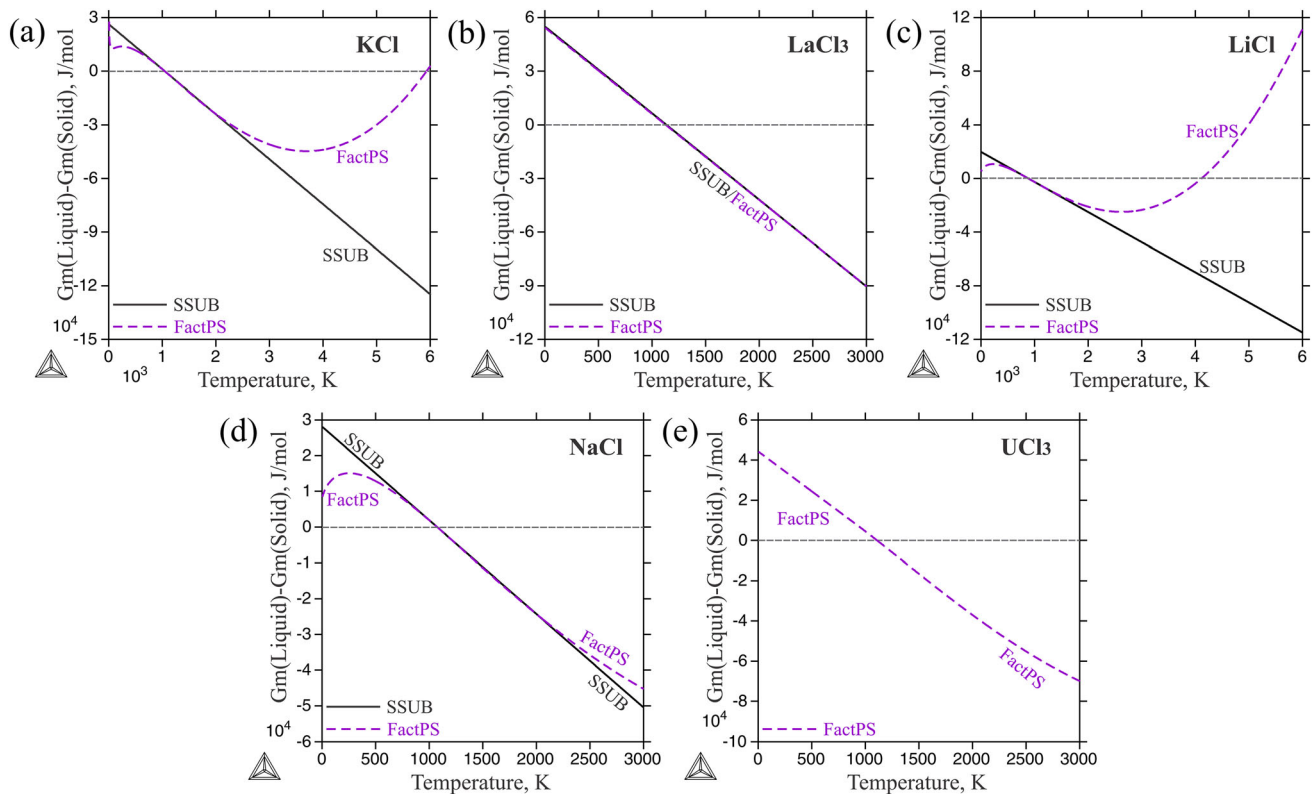


Fig. 5 Comparison of Gibbs energy between CALPHAD model-prediction using the FactPS and SSUB databases of pure salts: (a) KCl, (b) LaCl₃, (c) LiCl, (d) NaCl, and (e) UCl₃. In the plot, the solid phase is the reference state. Since the SSUB database does not

contain thermodynamic parameters of Gibbs energy for the liquid phase of UCl₃, subfigure (e) only shows the calculation based on the FactPS database

approach requires a comprehensive multicomponent database, even based on a low-fidelity thermodynamic description of the unary salts. Similar to the SGTE pure element database^[5] such an effort would be more like a standard development and requires to be organized.

As a short-term solution, at least, whenever there is a choice between databases, a comprehensive comparison for the unary salts should be executed before the assessment of binary and higher order systems. In this work, for the database development of the multicomponent salt, KCl, LaCl₃, LiCl, NaCl, and UCl₃, SSUB has been identified as the preferred database for the unaries. However, such a short-term action can only be based on the condition until a database for unary salts becomes openly available.

As a mid-term action, the CALPHAD community needs to interact with the molten salt community for the update of the unary CALPHAD database with better reproduction of the thermodynamic quantities, mainly heat capacity. The molten salt researchers, in principle, can provide more evaluations and experimental data to support the thermodynamic description of the unary salts. The creation of a data repository will be critical since the current CALPHAD unary model is still based on polynomial fitting, and efforts

are underway to employ a more physics-based model for unaries.

In terms of a long-term action, there could be a synergy when developing the new generation of descriptions for the metal systems. One can expect that models applied to metals can be extended to the molten salt systems, especially much of the ongoing atomistic modeling of molten salt systems can further support such a CALPHAD modeling effort when experiments are challenging to perform. Recently, efforts have been made on improving the descriptions of pure elements^[33–36] be more accurate in both low temperatures down to zero Kelvin and high temperatures above melting point and is highly desirable to apply the same approach for the description of unary substances.

With the ongoing efforts of automation of the CALPHAD assessment,^[9] the database refinement will be much easier. Therefore, as long as the experimental data repositories are available,^[37] a high-quality unary database with new physics-based models can be developed readily.

5 Conclusions

- In this work, the comparison of thermodynamic properties of the selected salts between SSUB and FactPS databases reveals the fundamental issues in the multi-component molten salt database development.
- The SSUB database released by the SGTE is more suited as the basis for the development of a thermodynamic database including the salts evaluated in the present work. However, a much more sustainable long-term solution is to carefully assess the unary molten salts with reported experimental work and supportive atomistic modeling, for example, density functional theory calculations and make this database openly available. Such an effort will foster further application and improvement of the CALPHAD approach.
- Although a considerable amount of thermodynamic modeling has been performed for the molten salt systems, we are still at the early stage of developing the CALPHAD database for molten salt applications. Therefore, the identified issues of the unary salts should be solved in a timely manner through the collaboration between molten salt and CALPHAD communities.
- The present work focuses on a molten salt system, but it is likely that similar issues related to the thermodynamic models of the unary exist in other non-metallic systems, such as oxides. The CALPHAD community should realize the critical need for further improvement of the unary databases. Furthermore, a unary database for diffusivities with high fidelity is also lacking when developing multicomponent atomic mobility databases.
- The ongoing development of materials informatics, including its computational tools and database assessment automation, will significantly reduce the efforts in future database development. However, ensuring a healthy CALPHAD tree with a high-quality unary database is essential and should be carried out without hesitation.

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