An Alternative Strategy for Thermodynamic Evaluations of Experimental U-Me Phase Diagrams to Resolve Considerable Experimental Discrepancies

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Abstract

Post irradiation examinations of burned-up nuclear fuels reveal a host of fission products. The changing chemistry of the fuel has effects on the deformation of fuel pellets and interactions with the cladding. Thus, mechanisms of various types of corrosions have been the focus of both experimental and thermodynamic investigations during the past decades. The construction of uranium related experimental phase diagrams are time consuming, costly, and fraught with many technical difficulties (*e.g.*, accuracy in high temperature measurements and contamination of samples by crucible materials). Both effects have been found in the experimentally constructed phase diagrams for U-Me systems (where Me = Ru, Rh, and Pd). The experimental discrepancies become apparent as the Me component changes from Ru to Pd. Resolving the discrepancies in these three systems has led to an alternative strategy being developed for the optimization of phase boundaries and identification of experimental fallacies.

1. Introduction

Today, the principles of computational thermodynamics are extensively recognized. There are many different kinds of software available for phase diagram calculations, among which the most widely used software may be Thermo-Calc. In order to accelerate the optimization process, optimizers, such as Carrol, are frequently used. In FactSage, an optimizer, called OptiSage is also available. While the optimizers may accelerate optimization processes, the expertise of the assessors is still essential for good practice because of the complexity of experimental data. In many experimentally constructed phase diagrams, repeated experimental data are rare in some instances. In others, some of the main features of these phase diagrams, *e.g.*, eutectic temperatures or compositions, are very different. It is important to determine how these differences in experimental data affects the optimization and to what extent subjective judgements affect the result. Another question to explore is whether it is possible to identify erroneous experimental data in the controversial phase diagrams by means of a thermodynamic evaluation. The answers to these questions are critical for a successful assessment. This paper will focus on an alternative strategy in coping with these questions.

2. Present practice and the necessity for a strategy change

Currently, most thermodynamically described alloy systems are systems with relatively low melting points of the components, for example, non-transitional metals. For these systems, the temperature measurement techniques are sophisticated, the repetition of the phase boundary measurements is good and no apparent crucible contamination is observed. Therefore, the use of an optimizer is helpful, although expertise is still a key for the optimization. However, for systems involving refractory metals, the situation is quite different. In thermodynamic evaluation of the U-Me systems, it is found that a Gibbs energy optimizer coupled with an optimizer has difficulties in dealing with such systems.

2.1 Present practice and its advantages and disadvantages

2.1.1 Widely used optimization procedures

According to some introductory papers, in the CALPHAD[1] method a Gibbs energy minimizer (*e.g.*, the Thermo-Calc) is directly coupled with an optimizer. For example, Kumar and Wollants presented a flowchart describing the general CALPHAD approach [1], which is sometimes referred to as the coupled thermodynamic phase diagram analysis:

[1] The word CALPHAD is an acronym from "CALculation of PHAse Diagrams." Therefore, thermodynamic calculations with different software should be covered under it. However, in practice, the word usually refers to Thermo-Calc coupled with Carrol software because of its extensive use.

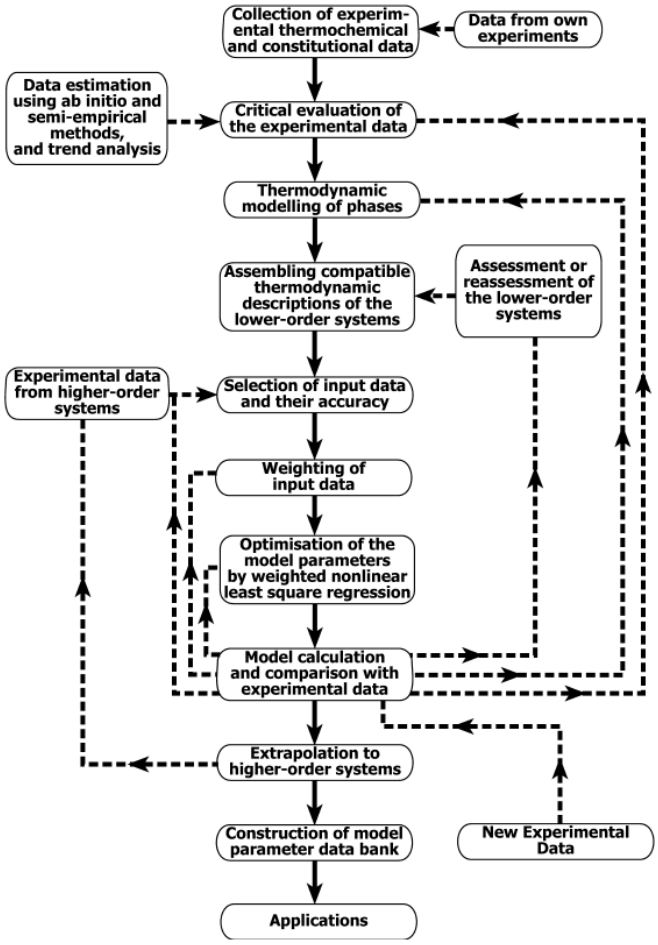

Figure 1. A flowchart of CALPHAD method by Kumar and Wollants.

In this approach a pure mathematical program using "weighted nonlinear least square regression" is incorporated with the Gibbs energy minimizer and different sets of experimental data have to be "weighted" subjectively prior to the optimization process. In dealing with a controversial system, such as that of U-Pd, the weighting of the controversial experimental data prior to the optimization is difficult. One may have to do them separately for each version of the phase diagrams and yet may not know which of them is the most acceptable even after all the different versions have been assessed. It is true that, without experimental data, a thermodynamic model will have nothing to be based on. On the other aspect, an experiment might not be perfectly designed or, during the process, some unexpected factor might have led to a considerable deviation of the experimental result. Therefore, a successful thermodynamic evaluation should be able to deal with such worst scenarios.

2.1.2 Advantages and disadvantages of the widely used procedures

During the past half century, the CALPHAD method has found its application in many fields, especially in various kinds of materials design, including plastics, porcelain, steel, and other

characteristic alloys. In nuclear engineering, thermodynamic evaluation of phase diagrams provides valuable information for nuclear material design and fabrication, as well as studies on nuclear fission products. Valuable lattice stability databank (Gibbs energy expressions of almost all stable elements as a function of temperature) have been established and verified by applications in different materials systems. As a result, the data in databanks such as the SGTE (Scientific Group Thermodata Europe) databank are becoming more and more reliable and have strong potential in evaluating an anomaly or even a series of bad experimental points on a phase diagram. As for thermodynamic principles, Gibbs had laid down almost all the basic laws and equations approximately 150 years ago [2]. Van Laar [3, 4] tried to apply the principles in phase diagram calculations, but the true breakthrough came only around the 1970s when computer techniques were becoming sophisticated. As mentioned before, in present phase diagram calculations the introduction of the pure mathematical least square regression may twist a pure thermodynamic calculation and produce multiple solutions of Gibbs energy functions of the solution phases. Consequently, for a phase diagram calculation, different configurations of interaction parameters may be obtained in different iterations, although a very similar phase diagram can be obtained. This deteriorates the function of thermodynamic evaluations. In order to avoid this, extra experimental thermodynamic properties, such as enthalpy of mixing and entropy of mixing or activities of a liquid at equilibrium (the liquidus), are needed. Nevertheless, for species involving high temperature measurements, the determinations of these quantities usually are problematic [5]. This is why many experimental thermodynamic properties are missing.

In U-Me subsystems, lack of thermodynamic data is not uncommon. For example, parts of the liquidus of U-Ru, U-Rh and U-Pd systems are uncertain. This can be seen from the dash-lines representing liquidus in the phase diagrams. It is more difficult, if not impossible, to measure the enthalpy and entropy of mixing for these parts of liquidus because the systems are very different from those of electrolytes at room temperatures. Therefore, an alternative method needs to be found.

2.2 The necessity of a strategy change

2.2.1 Significance of solution phase diagrams

In this work, FactSage [6] is used as the tool. The software is designed for assessors who are not programmers; nevertheless, a deep comprehension of the thermodynamic principles and expertise of the assessment are indispensable. In FactSage, Phase Diagram and OptiSage are two separate modules, but they can be combined by establishing a ChemSage file. In this way, an optimizing process, such as the one shown in Figure 1, can be realized. However, because of the excessive numbers of unknown properties and interaction parameters, it is very difficult to obtain converged values by direct coupling of the two modules. In addition, the calculation time in each trial is very long. In short, the optimization process is no less time consuming than the new strategy established in this work and often guideless or even fruitless for systems like the U-Me systems.

In order to cope with these difficulties, establishment of a metastable solution phase diagram was attempted for each of the U-Me systems. This involves the establishment of phase boundaries of the solution phases in a targeted binary system in which the liquidus and solidus

are stable in the experimental phase diagram. Because the existence of intermetallic compounds (in each of the three U-Me systems, there are four or five compounds), the shape of the middle part of the liquidus is not important in the solution phase diagram because it will change as the intermetallic compounds are added. However, parts of the U-rich side and the Me-rich side will not be affected and thus can serve as benchmarks in calibrating the liquidus. This solution phase diagram is sorted out at specific lattice parameters by optimizing the solution phase interaction parameters. The interaction parameters sensitively change the shape of the phase diagram, and it is found to be unique, *i.e.*, no multiple solution problem.

While trying to keep the calculated phase boundaries as close as possible to experimental liquidus and solidus by trial and error, other related solution phase boundaries below the liquidus and solidus are created in the same way by examining the phase relations through the experimental phase diagram (or diagrams if more than one version is available). These boundaries need not agree with their experimental counterparts before the compounds are accommodated but they must agree or be close enough to the experimental boundaries after that.

In FactSage, the solution phase database is established after the creation of the compound database. The lattice stabilities must be carefully chosen and hypothetical lattice stabilities should be cited whenever possible. If not, approximate values can be adopted, for instance, a value calculated by the *ab initio* method [7]. When this kind of value is not available, an estimation is needed by comparison of the lattice stabilities of similar phases of neighboring elements or calculation from an existing Gibbs energy expression by specifying a proper constant temperature.

Another advantage of this approach is that it is possible to judge the proper position of the liquidus even though some thermodynamic properties are missing. This is achieved by plotting the solution phase diagrams with different a_0 value of the liquid phase in combination of the fitness of the liquidus on both sides with experimental data. This is because, in Margules formalism, the first term of the polynomial weighs most and other terms become trivial as the product of the mole fractions become smaller and smaller and the exponent in the polynomial increases. One of the most important reference points is the minimum equilibrium value of the Me-rich side liquid-*cph* phases in U-Rh phase diagram or liquid-*fcc* phases in U-Pd phase diagram depending on the stable crystal structure of the Me element. To summarize, a solution phase diagram provides useful information for estimating a reasonable position of the liquidus where enthalpy and entropy of mixing values are missing and it is the frame work for construction of the whole diagram.

2.2.2 The function of experimental data and its relation to theory

In discussing experimental data analysis, Hughes and Hase quoted a statement from Richard Feynman, the Nobel Laureate: “The principles of science, the definition, almost, is the following: the test of all knowledge is experiment. Experiment is the sole judge of scientific ‘truth’.” [8] The theories, including the principles of science and definitions, originate from the observations upon natural phenomena or the results of designed experiments. Without experiments there would be no theories. On the other hand, the experiments must be carefully designed and conducted, and the results must be thoroughly examined when it is correlated

with a theory. Before declaring an experiment is complete and the results are sound, the results must be proved to be reproducible. In addition, it is necessary to check if a new phenomenon or effect is observed or omitted in the process.

Generally, the relation between experiments and theories is that the former are the basis of the latter; however, when the former is doubtful or controversial, a false theory may be derived. The types of experimental error can be classified into three main categories:

1. Random error
2. Systematic error
3. Anomaly/anomalies (Bad data point(s))

The first two types of errors can be managed by data analysis; however, the anomalies are sometimes misinterpreted and neglected because the causes may be unpredictable and they might be new phenomena that have never been observed or previously noticed.

In phase diagram construction, especially in phase diagrams involving transition metals, high temperature measurements and contamination by the sample containers (*e.g.*, the crucibles) impose detrimental challenges.

As shown in Figure 1, for different data sets, data weighting is performed prior to the optimization in the CALPHAD method. Because "the selection and weighting of the data are very subjective [1]," it can be fatal to the successive optimization if an anomaly or even anomalies are included in the data sets. As can be seen from the flowchart, the procedures are more experimental data targeted, which is reasonable for systems that are well studied and involve relatively low temperature measurements, *e.g.*, Mg-Ca (<1000 °C), Mg-Sr (<800 °C), and Al-Sr (<1100 °C) systems [9]. However, this procedure may be difficult in dealing with systems that are sparsely investigated by experiments and systems with possible contamination issues, *e.g.*, U-Rh and U-Pd systems. Because of the sparsity and controversy of the experimental data, thermodynamic evaluations of the systems become more important. In order to emphasize the necessity of theory evaluation and distinguish different treatments to well-studied and not well studied systems, some previously used terms need to be redefined. For the latter, the concept of "thermodynamic evaluation" (theory dominated) should be used, rather than "thermodynamic modelling" (experimental targeted).

Therefore, the function of experimental data should not always be the benchmark of thermodynamic assessment, especially when considerable discrepancies exist. When the system is complicated and very high temperature measurements are involved, the different sets of data should be referenced during the optimization process, but should not be directly involved in optimization processes. For this purpose, establishment of a solution phase relationship prior to adding the compounds are necessary. This is the main difference between this work and the frequently used procedures shown in Figure 1.

Thermodynamicists have discussed the influence of non-random errors of data on the optimization results of modelling, for example, Schmid-Fetzer *et al*. discussed the issues of accuracy, reasonability and safety of a dataset [10]. In an introduction to thermodynamic optimization of phase diagrams, Saunders and Miodownik quoted a dialogue in a question-and-answer session on this issue in 1995 [11, p. 285]. The questioner asked about the

possibility of identifying a faulty measurement by thermodynamic evaluation in existence of several distinct measurements of a phase diagram. Saunders replied that the answer is both yes and no. When all experimentation is reliable and of good quality, the resulting liquidus will give confident limits. However, it is not always the case that the experimentation is of good quality. For high-melting-point systems, experimental data are often unreliable. He confirmed that "CALPHAD calculation does impose a self-consistency" and can be used to identify a faulty measurement. Because of the general nature of the discussion, it is uncertain if the same procedure shown in Figure 1 was used in selecting a faulty measurement, or if the identifications are very difficult because of the lack of a guidance by a solution phase diagram.

2.2.3 Reliability of lattice stabilities

A solution phase diagram for evaluation of experimental data should be based on sound built lattice stabilities. The development of lattice stability data began in the post-war period [11, p. 7]. For many years, the pioneering work in computational thermodynamics was very difficult for experimental thermodynamicists to accept. Finally, Koffman and Bernstein published *Computer Calculations of Phase Diagrams* in 1970, which was translated into several languages within a few years. The first International CALPHAD Conference was held in Boston in 1973 and now occurs annually. In 1977, the first volume of the CALPHAD journal was published. Since then, a large number of papers on thermodynamic calculations of phase diagrams have been presented at the conferences and published in the journal. In the meantime, lattice stability data for most elements of interest have been elaborated. In 1991, Dinsdale summarized and published comprehensive set of unary thermodynamic data of elements in CALPHAD [12] and, since then, the database has been updated from time to time and widely used. While it is still being improved, some systems have been sophisticated both in experiments and thermodynamic analyses, with the result that the lattice stability data of the elements are very reliable for describing new binary systems and extrapolating to higher order systems.

In constituting a solution phase diagram, or as it is sometimes referred to, a metastable phase diagram, lattice stability data are essential. When a hypothetical lattice stability is needed, the first option is to cite from a reliable source; the second option is to use a calculated value, such as one by the *ab initio* method [7]; the third option is to estimate the value by comparing available values of the neighboring elements. Hypothetical lattice stabilities are necessary for the thermodynamic calculation of a phase diagram but, because they are metastable in nature, they do not affect the determination of stable phase boundaries. However, in a multicomponent model the hypothetical value for the element in the same crystal structure in different systems must remain the same. For example, in U-Rh and U-Pd subsystems, U does not exist as an *fcc* crystal structure but the *fcc* phase is stable for both Rh and Pd; consequently, in thermodynamic calculations of U-Rh and U-Pd phase diagrams a hypothetical *fcc* lattice stability for U has to be provided. The value determined chosen from one of the three options discussed above should be in agreement in all these subsystems.

In a phase diagram, the boundaries of phases can be basically classified into three types:

1. Boundary of a solution phase in equilibrium with another solution phase or a compound phase; *e.g.*, liquidus, solidus or solvus.
2. Boundary of a stoichiometric compound. This kind of boundary is independent of composition, *e.g.*, a vertical line representing a compound of U_xMe_y. This kind of boundary can be either in equilibrium with another compound or with a solution phase.
3. Boundary of a non-stoichiometric compound. For this kind of boundary the Gibbs energy of the compound is a function of both temperature and composition, although sometimes the composition range is very narrow. Similar to type 2, this kind of boundary can be either in equilibrium with another compound or a solution phase. All the binary compounds are treated as stoichiometric compounds.

The boundaries of type 1 are determined by the solution phase diagram of a complicated system with compounds. The features of the liquidus close to the two terminal elements are the most important parts of the phase diagram because the trends of the liquidus and solidus define the basic relations among the solution phases in equilibrium. In a U-Me system, the U-rich part of the liquidus is usually more accurately determined than the Me-rich part of the liquidus because of the lower melting point of U. The certainty of experimental data always determines the soundness of a thermodynamic modelling or evaluation. However, for a system with sound lattice stability data, but with considerable discrepancies in the phase diagrams from several groups of experimentalists, a thermodynamic evaluation by a solution phase diagram with reliable lattice stabilities will be much more convenient and reliable than subjective weighting of experimental data prior to the optimization step for these kinds of systems.

3. Procedures adopted in thermodynamic evaluations in U-Ru-Rh-Pd quaternary system

On the basis of the foregoing discussion, the coupling mode of Phase Diagram and OptiSage modules by generating a ChemSage File in FactSage, a procedure similar to the one shown in Figure 1, is not adopted in this work. Instead, a direct error and trial method involving two separate cycles, as shown in Figure 2, is attempted.

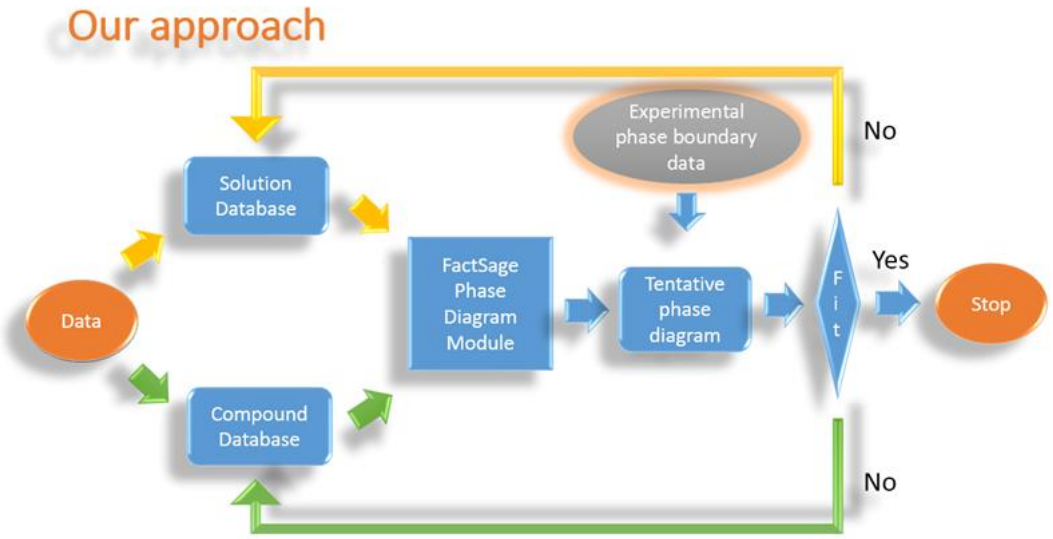

Figure 2. Schedules adopted in this work.

In Figure 2, upon establishing the compound and solution databases, the Phase Diagram module is used in searching for a tentative phase diagram. All the available experimental phase diagram data points are plotted in separate files with corresponding coordinates for different systems. These data points can be superimposed with the tentative phase diagram whenever needed for a comparison. Therefore, the data are not directly involved in an optimization processes and an assessor does not need to judge subjectively before or during the optimization. Furthermore, by this means, all the existing experimental data can be reasonably considered during an optimization process.

The blue arrows in the flowchart represent directions for both of the sub-cycles. The yellow arrows form the first cycle together with some of the blue arrows for optimization of a solution phase diagram. This process is time consuming. Usually, it takes about two thirds of time involved in optimizing a whole binary system. In addition, extra expertise is necessary in judging the final shape of the solution phase diagram. For example, in the U-Rh system, five solution phases are involved: the liquid phase, α-U, β-U and γ-U solid solutions, and Pd-rich *fcc* solid solution. The solution phase diagram should show all the phases and the phase transformation features of the system, although most parts of the phase boundaries are metastable. Figure 3 is an optimized U-Rh solution phase diagram. In this diagram, the equilibria between the liquid and γ-U (*bcc*) phases, liquid and *fcc* phases, γ-U and β-U phases, β-U and α-U phases and α-U, β-U, γ-U and *fcc* phases are illustrated.

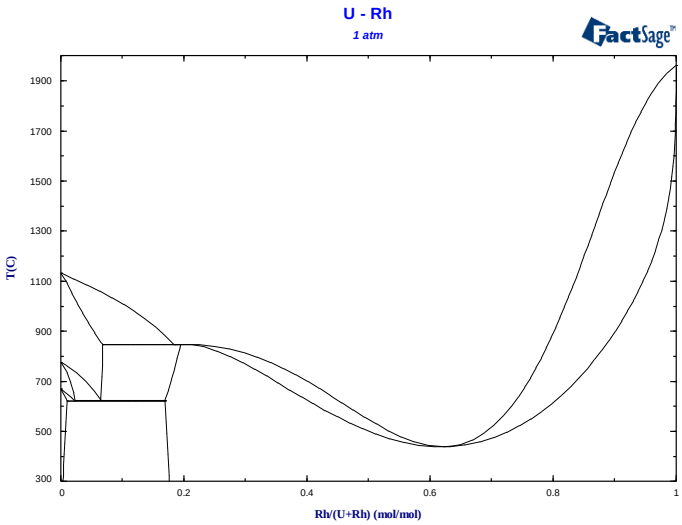

Figure 3. The optimized solution phase diagram of U-Rh binary system.

Once a satisfactory solution phase diagram is obtained, the interaction parameters for the solution database are determined. Unless there are specific reasons, no dramatic adjustments will be needed.

The second cycle then begins, which is represented by the green arrows together with some of the blue ones. The compounds in a system are added one by one. In U-Me systems, the UMe_3 compounds have been extensively studied and their thermodynamic properties, such as enthalpy of formation, entropy and heat capacity, are available from the literature; therefore, they can be good starting points (Figure 4) for establishing these systems. Because the liquidus has been optimized prior to the accommodation of the compounds, it can be used as a benchmark in evaluating different experimental thermodynamic properties, *e.g.*, enthalpies of formation of the compounds for a system with considerable deviations among different sources. At the same time, other compounds with no known thermodynamic properties can be accommodated and their thermodynamic properties can be calculated or estimated.

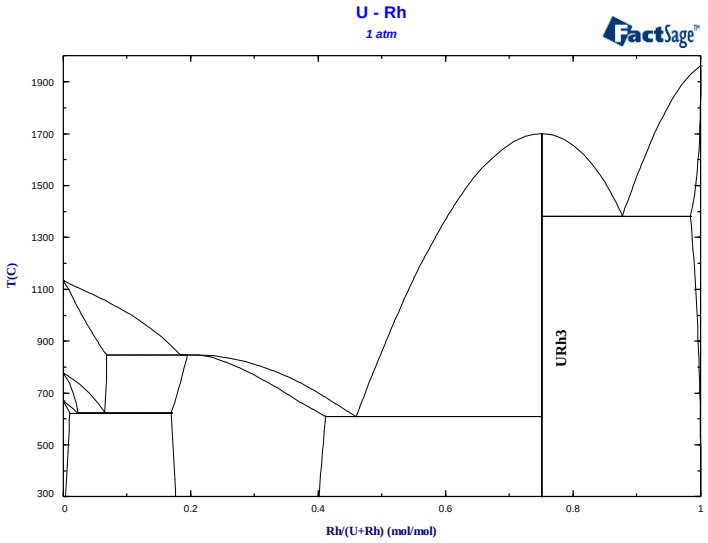

Figure 4. A calculated U-Rh phase diagram with URh_3 added.

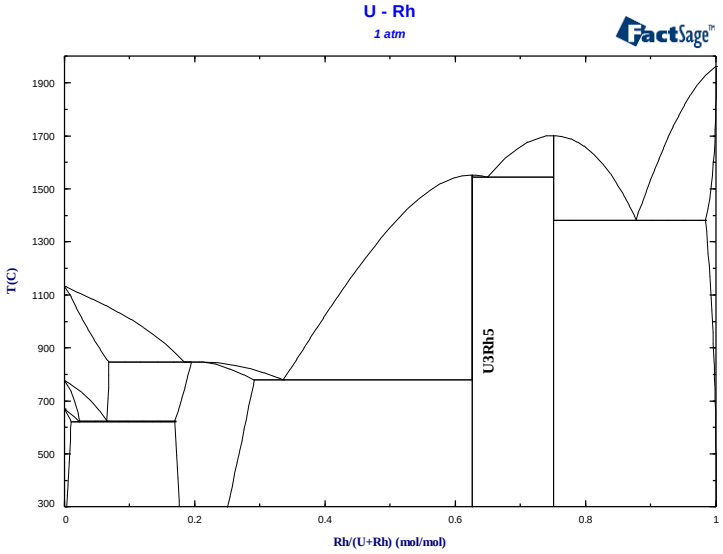

Figure 5. A calculated U-Rh phase diagram with U_3Rh_5 added.

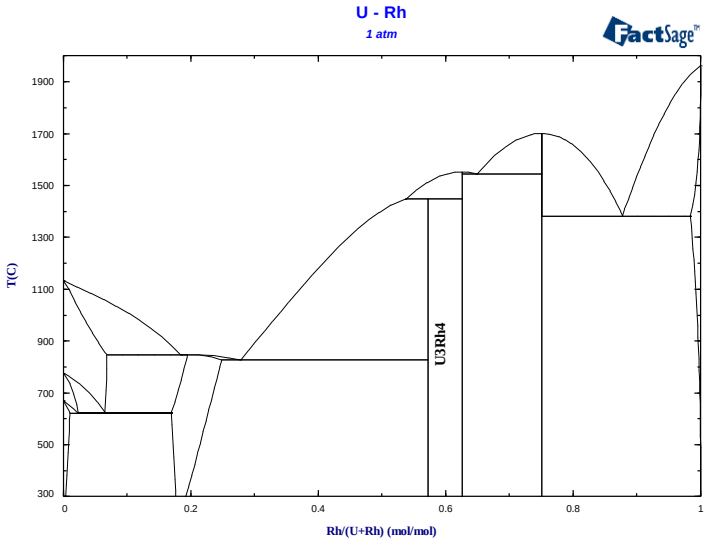

Figure 6. A calculated U-Rh phase diagram with U_3Rh_4 added.

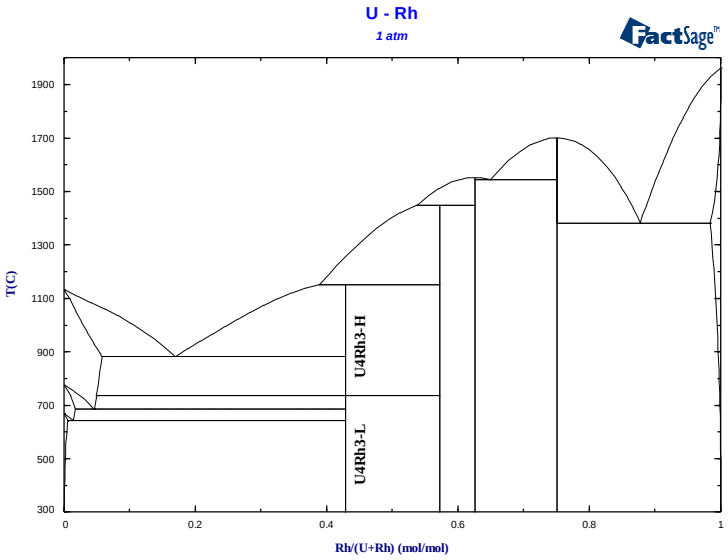

Figure 7. A calculated U-Rh phase diagram with U_4Rh_3 added.

With the final compound (U_4Rh_3) added (Figure 7), the calculated U-Rh phase diagram exhibits all the main features of its experimental counterpart. At this stage, some minor adjustments may be needed, both for the solution phase boundaries and the compound boundaries. Figure 8 shows the final calculated U-Rh phase diagram. Nevertheless, the "final" calculated phase diagram is always a result of a compromise between different sets of experimental data and different calculated results. In some circumstances, one may find that some experimental data could not simply be "simulated" by the thermodynamic calculation. For instance, in the U-Rh phase diagram evaluation, the experimentally "determined" U-rich side eutectic composition could not be obtained in the thermodynamic calculation. This may

suggest that the interpretation of an adjacent experimental datum by the experimentalist should be questioned and re-examined.

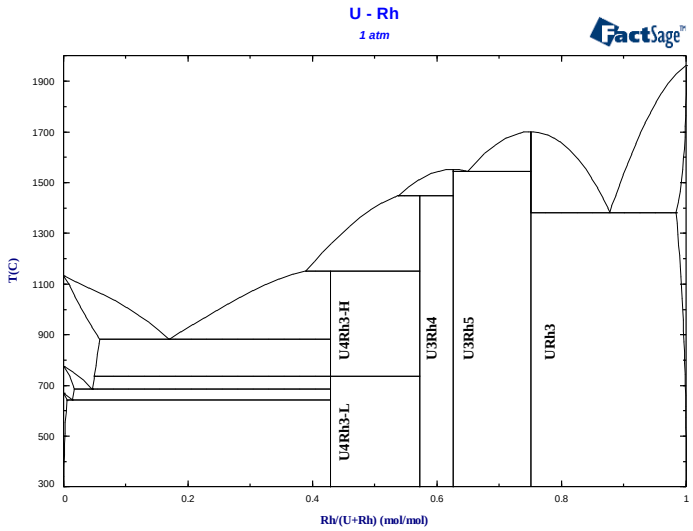

Figure 8. The final calculated U-Rh phase diagram.

Figure 9 shows the way the liquidus changes during the addition of the compounds although the solution interaction parameters are not changed during the addition of the compounds.

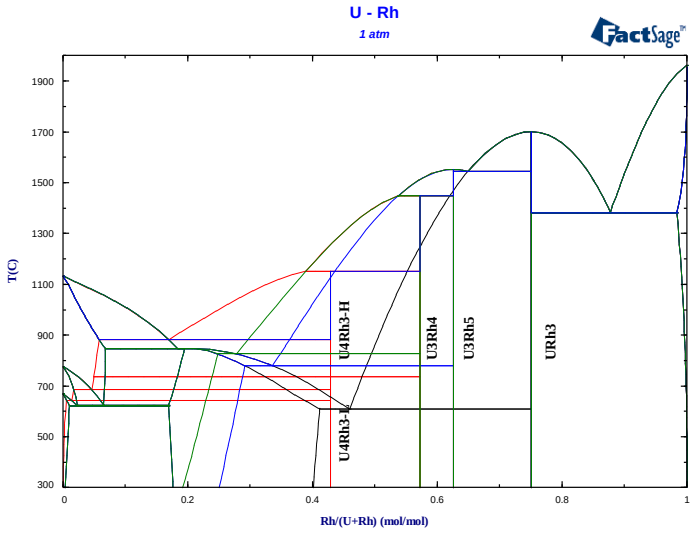

Figure 9. The shape of the liquidus changes as the compounds are added.

4. Conclusion

In order to deal with difficulties in assessments of controversial systems, *i.e.*, systems with obvious differences from different sources; an alternative approach in FactSage is adopted.

The new procedures can avoid errors that might be caused by subjective weighting of experimental data prior to optimization, which is a commonly used procedure in CALPHAD practice. It is worth emphasizing that, the original procedure is good for well-studied phase diagrams, that is, phase diagrams with agreeable experimental phase boundary data from different experimentalists. These systems usually consist of elements with low melting points or the electronic structures of the elements are stable. The procedure is purely experimental data targeted, and therefore cannot be used for systems such as the U-Rh and U-Pd phase diagrams included in the thermodynamic analysis of the U-Ru-Rh-Pd quaternary system because of the high catalytic efficiency of Pd and the contamination effect of the beryllia crucibles used in the phase diagram determinations. A paper on the quaternary system will also be presented on the 36th Annual Conference of the Canadian Nuclear Society.

5. References

[1] K.C. Hari Kumar, P. Wollants, "Some guidelines for thermodynamic optimisation of phase diagrams," *Journal of Alloys and Compounds,* vol. 320, 2001, pp. 189-198.

[2] J. Gibbs, "Scientific Papers of J. Willard Gibbs", Vol. 1&2, 1906, London, New York and Bombay: Longmans, Green and Co.

[3] J. v. Laar, *Z. Physik. Chem.,* vol. 63, 1908, p. 216.

[4] J. v. Laar, *Z. Physik. Chem.*, vol. 64, 1908, p. 257.

[5] H. L. Lukas, S.G. Fries and B. Sundman, "Computational Thermodynamics: The Calphad Method", Cambridge: Cambridge University Press, 2007, pp. 110-111.

[6] C.W. Bale *et al.*, "FactSage thermochemical software and databases - recent developments," *CALPHAD,* vol. 33, 2009, pp. 295-311.

[7] M. Sluiter, "*Ab initio* lattice stabilities of some elemental complex structures," *CALPHAD,* vol. 30, 2006, pp. 357-366.

[8] I.G. Hughes, T.P.A. Hase, "Measurements and Their Uncertainties: A practical guide to modern error analysis", Oxford: Oxford University Press, 2010, p. 1.

[9] M. Aljarrah, "Thermodynamic Modelling and Experimental Investigation of the Mg-Al-Ca-Sr Systems", Montreal: Concordia University, 2008.

[10] R. Schmid-Fetzer *et al*., "Assessment techiques, data design and software facilities for thermodynamics and diffusion," *CALPHD,* vol. 31, 2007, pp. 38-52.

[11] N. Saunders and A.P. Miodownik, "CALPHAD: A Comprehensive Guide, Oxford, New York and Tokyo: Elsevier Science Ltd., 1998.

[12] A. Dinsdale, "SGTE data for pure elements," *CALPHAD,* vol. 15, no. 4, 1991, pp. 317-425.