Editorial

One cannot overemphasize the importance of phase diagrams in materials research. They are the road maps for materials scientists/engineers in alloy design and development. Experimentally determined phase diagrams are mainly for binary and ternary systems, while the CALPHAD method plays an important role in obtaining multi-component phase diagrams. In this approach, separately measured phase equilibrium data and thermodynamic properties are converted to a unique thermodynamic description of the system in question. This thermodynamic description can be used to not only reproduce the known properties, but also to predict the unknown properties of the system. More importantly, thermodynamic descriptions of the constituent binaries and ternaries can be combined and extrapolated on the basis of geometric models to develop a thermodynamic description of a multi-component system. The term "thermodynamic database" or "database" is usually used for a multi-component system instead of "thermodynamic description." The ultimate goal of the CALPHAD approach is to use the thermodynamic database such developed to predict phase equilibria and thermodynamic properties of a multi-component system that are usually not experimentally available. There is no doubt regarding the potential power of the CALPHAD approach; by using this approach, a tremendous amount of experimental work can be saved. Indeed, many applications have been developed on the basis of phase diagram calculation in the past few decades. Regardless of its success, continuous efforts are needed to improve the accuracy of the multi-component thermodynamic databases, which is the key for the successful application of the CALPHAD approach.

In this editorial, I would like to touch base regarding two major points that I think both thermodynamic database developers and users should be aware of: (1) the composition limit of the database, and (2) the role of metastable phases. The strategy of building a thermodynamic database for an alloy system with n components starts with deriving thermodynamic descriptions for all the constituent binary and ternary systems. There are C_n^2 constituent binaries and C_n^3 ternaries in an n-component alloy system, where $C_n^i \equiv \frac{n!}{i!(n-i)!}$. After thermodynamic descriptions for all the constituent binaries and ternaries are developed, a multi-component thermodynamic database can be established. High order interaction parameters are usually not necessary, since although interactions between binary components are strong, ternary interactions are weaker, and they become significantly weaker in higher ordered systems. Certainly, if a new phase forms in the multi-component system, thermodynamic model and model parameters should be developed for this phase. Building a multi-component thermodynamic database is like constructing a puzzle. If each small piece of the puzzle (low order systems) is put in place, the whole picture (multi-component system) is clearly revealed. However, development of a complete database for a multi-component system with more than 10 components is usually not accomplishable due to the large number of subsystems. For example, to develop a database with 15 components, 105 binaries and 455 ternaries need to be modeled, and some of the quaternaries may need to be considered as well. Even more challenging, thermodynamic descriptions for many ternaries and some binaries cannot be developed due to the lack of experimental information. As a result, current multi-component thermodynamic database is usually constructed at the corner of the major elements, focusing only on key systems that are important for industrial applications and have abundant experimental information. This is like a partially finished puzzle. Application to composition ranges that are outside what these key systems have to offer can therefore be risky.

The other issue requiring address concerns the metastable phases. When a thermodynamic description is developed for a binary or ternary system, Gibbs energy functions are optimized only for the phases that are stable in a particular system. Metastable phases are usually not considered due to the fact that experimental data are rarely available for these phases. Neglect of metastable phases causes no problems for the lower order system since these phases are behind the scene. However, it does raise issues in the multi-component system, in which the Gibbs energy, of a phase is the weighted summation of those from the constituent lower order systems. The Gibbs energy of a phase in every constituent subsystem makes contribution to the total Gibbs energy, regardless of its stability in the subsystem. Less accurate Gibbs energies developed for the metastable phases in the subsystems certainly degrade the accuracy of the total Gibbs energy of a phase in the multi-component system, and makes the predictability of the multi-component thermodynamic database questionable. One example is the TCP phases in the nickel-based superalloys. TCP phases appear in many commercial nickel alloys, yet their Gibbs energies are not well developed in the multi-component system due to the above-mentioned reasons.

In summary, the successful application of the CALPHAD approach relies on the availability of high quality thermodynamic databases, which in turn depends on the trustworthy experimental data for the constituent binaries and ternaries. It should be kept in mind that Gibbs energy functions for the metastable phases are equally important as those of the stable phases, and ab initio calculation is essential in finding such values. While the development of reliable multi-component thermodynamic databases remains a challenge, close collaboration among experimentalists, thermodynamic database developers, and scientists working on ab initio calculation is the key to tackle this challenge.

Fan Zhang
Associate Editor
Journal of Phase Equilibria and Diffusion