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Assessment techniques, database design and software facilities for thermodynamics and diffusion

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Abstract

The purpose of this article is to give a set of recommendations to producers of assessed thermodynamic data, who may be involved in either the critical evaluation of limited chemical systems or the creation and dissemination of larger thermodynamic databases. Also, it is hoped that reviewers and editors of scientific publications in this field will find some of the information useful. Good practice in the assessment process is essential, particularly as datasets from many different sources may be combined together into a single database. With this in mind, we highlight some problems that can arise during the assessment process and we propose a quality assurance procedure. It is worth mentioning at this point, that the provision of reliable assessed thermodynamic data relies heavily on the availability of high quality experimental information. The different software packages for thermodynamics and diffusion are described here only briefly.

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1. Introduction

For more than 30 years, the Calphad method has proved to be an efficient tool for solving numerous problems in the field of materials research and thermochemistry. By using a step-wise approach, thermodynamic descriptions of unary, binary and higher order systems can be created and collected into large self-consistent databases allowing very complex equilibrium calculations to be performed for a variety of applications, from materials development to process control. The thermodynamic databases themselves contain assessed Gibbs energy parameters for thermodynamic models for the individual phases as functions of temperature, composition and pressure. The databases are then linked to software for the calculation of phase equilibria for the practical applications of interest. The success of the Calphad technique depends upon the reliability of these databases.

The purpose of this article is to give a set of recommendations to producers of assessed thermodynamic data, who may be involved in either the critical evaluation of limited chemical systems or the creation and dissemination of larger thermodynamic databases. Also, it is hoped that reviewers and editors of scientific publications in this field will find some of the information useful. Good practice in the assessment process is essential, particularly as datasets from many different sources may be combined together into a single database. With this in mind, we highlight some problems that can arise during the assessment process and we propose a quality assurance procedure. It is worth mentioning at this point, that the provision of reliable assessed thermodynamic data relies heavily on the availability of high quality experimental information. This aspect of thermodynamic assessment has been covered in detail previously [1] and [2].

Of course, the power of the Calphad technique is having the ability to perform calculations involving many components. This requires the creation of large databases for multicomponent systems; and this, itself, can pose problems that can trap the unwary. These issues are dealt with here.

The different software packages for thermodynamics and diffusion have been already described in depth in a special issue of the CALPHAD journal, vol. 26, iss. 2 (2002) pp. 141–312, and many of the packages are commercially available. These are described here only briefly.

2. Assessment techniques

2.1. Good assessment practice

2.1.1. Binary systems

2.1.1.1. Thermodynamic models

The first step in the development of a thermodynamic description of a binary system is to select model descriptions for the individual phases. In general, the choice of model depends on the crystal structure of the phase in order to reproduce the phase properties correctly. The choice of models will also affect how easily the description of this binary system can be combined with other binary systems for the calculation of higher order systems. For most of the disordered solution phases, such as liquid and terminal solid solutions, the choice of model is fairly straightforward. These phases are usually described by a substitutional solution model [3]. However, the existence of short range order phenomena in the liquid phase [4] or the formation of interstitial solutions require special treatment [5].

The choice of an appropriate model description for an ordered phase is influenced by a number of factors. One of the requirements is to reflect the arrangement of the atoms in the crystal structure and another is to keep the description as simple as possible. An overview of frequently encountered crystal structures is given in Section 3.2. In addition, an ordered phase may require special treatment if it takes part in an order/disorder transformation [6] and [7]. Ansara et al. [8] presented recommendations for the modeling of topologically close packed phases, while Ferro and Cacciamani [9] proposed a general strategy for the development of model descriptions of ordered phases. Hari Kumar and Wollants [2] discussed strategies for choosing appropriate model descriptions and refinement of the adjustable parameters. However, quite often the homogeneity range of a phase is found to be very narrow or the phase boundaries are poorly determined. In such cases, it is advisable to describe this phase as a stoichiometric compound.

A problem arises when experience from modeling ordered phases has resulted in improved model descriptions leading to an incompatibility between older and newer descriptions of a particular phase, thus preventing the combination of lower order systems for the extrapolation to higher order systems. To avoid such incompatibility it is advisable to model phases, such as the σ and μ phases, simultaneously with “old” and “new” model descriptions [10].

The accuracy level of an adjustable model parameter of a phase description depends on the breadth of experimental data as well as on the number of adjustable parameters. Therefore, it is mandatory for a good thermodynamic description that the minimum necessary number of adjustable parameters is used to correctly describe the system. In summary, the model descriptions chosen for the phases should reflect their features as accurately as possible while having the simplest description possible.

In addition to the choice of proper model descriptions, the choice of lattice stabilities is another important selection that must be made prior to the optimization process. Most of the lattice stabilities of the pure elements have been recommended by Dinsdale [11]. However, unknown lattice stabilities for the hypothetical end-member phases needed for the description of ordered phases must be estimated or possibly derived from ab initio calculations [12]. The choice of these end-member phase lattice stabilities is also of great importance for the compatibility with other systems for the calculation of higher order systems.

For stoichiometric compounds and end-member phases, care should be taken in order that the

thermodynamic description of the phase is realistic. Firstly, a decision has to be made regarding the reference state of the phase; should it be floating or fixed. For example, the Gibbs energy of a stoichiometric compound A_2B_3 using a floating reference can be written as follows:

$$G(A_2B_3, T) = 2^\circ G(A, T) + 3^\circ G(B, T) + (a + bT + \dots) \quad (1)$$

where $(a+bT+\dots)$ is the Gibbs energy of formation of the compound from the pure components at temperature T . This method is widely used because of its convenience, particularly if the only experimental thermodynamic data that are available relate to the enthalpy of formation of the compound. However, the disadvantage with this method is that any discontinuities in the C_p for the components, resulting from a phase transition for example, also appears in the C_p of the compound [7]. Using a fixed reference state can overcome these problems, where the Gibbs energy of the compound is now given as:

$$G(A_2B_3, T) = 2^\circ G(A, 298.15 \text{ K}) + 3^\circ G(B, 298.15 \text{ K}) + (a' + b'T + c'T \ln T + \dots) \quad (2)$$

where the c' and higher terms relate directly to the true C_p of the compound. Of course, this depends on the availability of experimentally determined C_p data for the compound.

Nevertheless, if this information is not available it can still be useful to use this approach by estimating a reasonable and continuous function of C_p for the compound, possible guided by Neumann–Kopp’s rule [13]. However, it is important to ensure that the estimated function does not force the compound to become stable at temperatures beyond its actual stability range.

2.1.1.2. Experimental data

It is highly desirable for the optimization of the thermodynamic description of a binary system that all *original experimental data* are critically evaluated and used during the optimization process. The use of *selected data* from phase diagram evaluations, such as presented by Massalski et al. [14], or thermodynamic data evaluations, such as from Hultgren et al. [15], limits the extent to which the consistency of phase equilibria data and thermodynamic data can be evaluated during the optimization process. For example, a data set may have been included in the evaluation of the thermodynamic data in spite of the fact that the values of these data are on the high or low end of the data spectrum. It may be, however, the optimization shows that such data set is consistent with the description that reproduces the phase equilibria data. This consistency check is even more hindered if “data points” from the digitization of lines of evaluated diagrams are used and, therefore, this should be considered poor practice.

It is important for a good assessment that only the originally measured data are used. This means that if partial thermodynamic quantities of one component have been measured that only these data and that neither derived integral quantities nor other derived partial quantities should be used. An exception can be made if the available experimental information is insufficient, then derived data could be used in place of estimated data if these data are assigned a low weight.

Lukas and Fries [1] described the optimization process for the thermodynamic description of the binary Mg–Zn system using the Lukas BINGSS program [16]. They discussed in detail the critical evaluation of experimental data, such as phase equilibria and enthalpy data, while Hari Kumar and Wollants [2] discussed partial Gibbs energy data. Ferro et al. [17] published an overview of the accuracy that can be expected from the various experimental methods used in the determination of phase equilibria and thermochemical quantities. Lukas and Fries also described error equations that are used in the optimization process and the role of the accuracy that was assigned to individual experimental values [1]. The accuracy or “error” of an experimental value

is of great importance for least-squares-type optimizations since it is directly linked to the weight with which it is used.

If certain quantities or temperature–composition regimes of a system are insufficiently defined by experimental data, estimates must be made or, if available, data from ab initio calculations can be used. The values from ab initio calculations depend strongly on the method used [12]. The variation in the values obtained from different ab initio methods can be treated similarly to the accuracy of an experimental measurement.

After the optimization of a system is complete the experimental data along with documentation of the optimization process should be saved electronically for future use and update. Documentation of the original optimization process will be of great benefit in case re-assessment of the system is needed. The need for critical experiments should be identified and documented.

2.1.2. Ternary and higher order systems

We want to describe in this section the different steps needed for the assessment of ternary systems.

First, it is necessary to check carefully the binary sub-systems according to the quality criteria defined below (see 2.2) and to re-assess them if necessary. Then, the ternary system has to be extrapolated from the binaries, considering all of the possible solution phases (liquid, terminal solid solutions) and binary intermediate compounds. No ternary interaction parameters should be introduced at this stage.

Different methods (Toop, Kohler, Colinet, Muggianu) [13] are available for extrapolating the excess Gibbs energy of a ternary solution phase from its binary values. The Muggianu method is used widely because no ternary weighting factors are needed for the extrapolation of Redlich–Kister polynomials with this method [13]. However, this may not be the best choice for the dilute solution of a chemically very different third component in a binary solution phase. The phase diagram then should be calculated and compared to the available experimental information.

Different cases may occur:

1. There are neither ternary compounds nor ternary solubilities in the binary compounds or terminal solid solution phases. In the case of inconsistency between calculated and experimental tie-lines, the binary systems should be re-assessed using additional constraints from the ternary system which may improve the relative Gibbs energies of the different phases.
2. Ternary compounds are identified in the literature: their thermodynamic data have to be assessed or estimated (enthalpy of formation, entropy, invariant reactions, decomposition or melting temperatures, etc.). The calculated tie-lines between the solid phases should be compared with experimental data. In the case of inconsistencies, the Gibbs energies of the ternary compounds should be adjusted.
3. Solubility in a binary intermediate phase or terminal solid solution may require the introduction of additional Gibbs energy terms into the thermodynamic model for this phase. These terms can be lattice stabilities of fictive end-members and/or interaction terms that may be estimated or possibly obtained via ab initio methods.
4. Remaining disagreements can be resolved by introducing ternary interaction parameters into the models of the relevant solution phases and assessing these parameters by using an appropriate method. The ternary interaction term itself can be understood as an interaction parameter between elements or components, as long as three pure elements are concerned. One typical case where this is almost always needed is when a miscibility gap is present in one binary system but not in

the other two. In this case, the extension of the miscibility gap into the ternary system is validated mainly by experimental information, and currently, no existing thermodynamic model has been able to reproduce it without the inclusion of ternary interaction parameters. Another typical case is that of oxide systems with strong interactions in the liquid phase together with binary and ternary solid compounds. In this case, binary and/or ternary associates may have to be introduced into the description of the liquid phase, and ternary interaction terms between these associates have to be estimated from available experimental phase diagram data.

Pelton [18] demonstrated the impact of different modeling procedures on the extrapolation of an A–B slag system with strong short range order in the liquid into an A–B–C system with weaker A–C and B–C interactions. The extrapolation produces a tendency for demixing in the ternary liquid phase that is (i) strongest when A–B is described using a Redlich–Kister polynomial (with extremely strong negative interactions), (ii) weakest when A–B is described as an associate solution and (iii) intermediate in strength when A–B is described using the quasi-chemical model. It was also shown that for many such slag systems, extrapolation using the quasi-chemical model comes close to observations of real systems, without introducing a ternary interaction parameter [18].

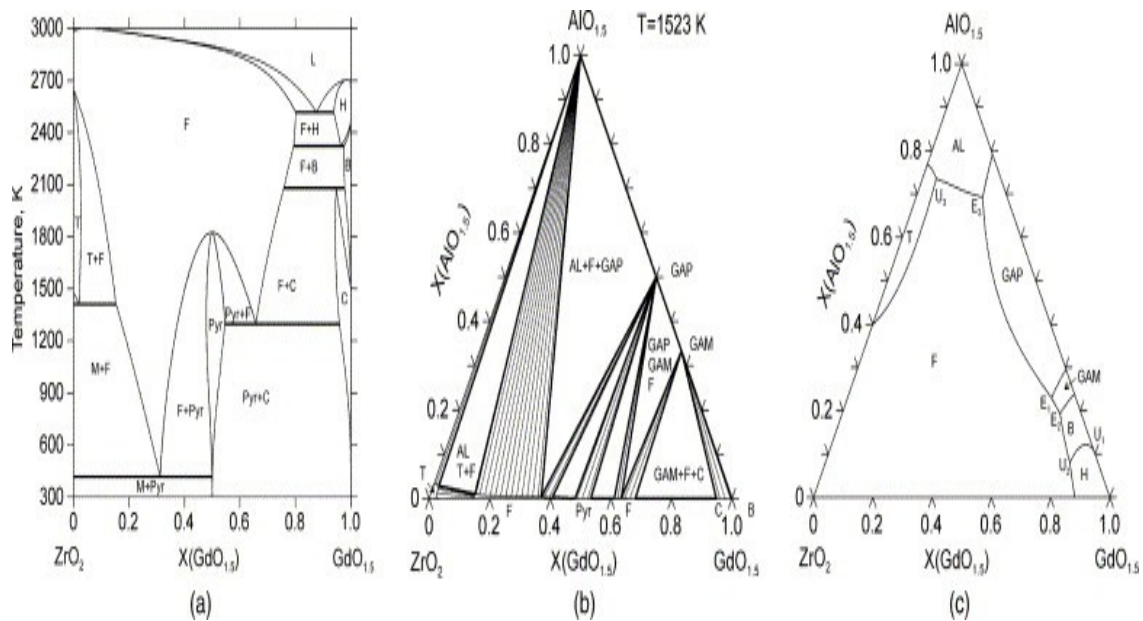
It should be emphasized that the ternary interaction parameters for liquid or other solution phases should be used with care. Their impact on activities can be quite counter-intuitive [19] and thus, ternary parameters should not be used for fitting the phase diagram without checking the activities, ideally in comparison to experimental data. In many cases, it is better to improve the binary description or the extrapolation method. The currently available optimization software packages will be described in Section 4; however if necessary, a specific method should be developed for a particular problem, which may result in using a more “manual” process than a virtually automatic procedure.

5. Remaining problems would indicate that thermodynamic remodeling should be considered. For example, a new species AlO_2^{-1} was introduced into the partial ionic liquid model in the MgO – Al_2O_3 – SiO_2 system in order to reproduce the limited miscibility gap in the liquid phase and other parts of the liquidus surface simultaneously [20].

The optimization of the $\text{AlO}_{1.5}$ – $\text{GdO}_{1.5}$ – ZrO_2 ternary system [21] is given in Fig. 1 as an example. By combining binary descriptions of the $\text{AlO}_{1.5}$ – ZrO_2 , $\text{GdO}_{1.5}$ – ZrO_2 and $\text{AlO}_{1.5}$ – $\text{GdO}_{1.5}$ systems, a set of thermodynamic parameters for the $\text{AlO}_{1.5}$ – $\text{GdO}_{1.5}$ – ZrO_2 system has been derived. It was shown that agreement between the calculated and experimental tie-lines in the ternary system depends on the temperatures of the eutectoid reactions $\text{F}=\text{M}+\text{Pyr}$ and $\text{F}=\text{C}+\text{Pyr}$ in the binary $\text{GdO}_{1.5}$ – ZrO_2 system (see the phase names in the captions to Fig. 1). These reactions were not studied experimentally because of difficulties in reaching equilibrium at low temperature. If the calculated temperatures of these reactions are not low enough the tie-lines between Pyr, F, corundum and the GAP phases contradict the experimental data in ternary systems at 1523 K. Therefore, phase relations in the ternary system allowed the authors to constrain the thermodynamic parameters in the binary system and to obtain the thermodynamic description of the solid phases in the $\text{AlO}_{1.5}$ – $\text{GdO}_{1.5}$ – ZrO_2 system. This description reproduces the experimental isothermal sections at 1473, 1523 and 1923 K. However, if ternary interaction parameters are not introduced into the description of the liquid phase it will already be stable at 1923 K which is in contradiction with the experimental observations. Without using ternary interaction parameters in the description of the liquid phase, the temperature of the eutectic reaction E_3 was calculated to be 77 K lower than determined experimentally. Therefore, a ternary interaction parameter was introduced in the liquid and optimized to fit the experimental data for

the liquidus surface; Fig. 1(c).

Fig. 1. Sequence of ternary optimization of the $\text{AlO}_{1.5}$ – $\text{GdO}_{1.5}$ – ZrO_2 system [21]. (a) pseudobinary edge ZrO_2 – $\text{GdO}_{1.5}$, (b) isothermal section at 1523 K, (c) liquidus surface. Phase designations: F — fluorite structure, T — tetragonal, M — monoclinic ZrO_2 -based solid solutions; C — cubic (bixbyite), B — monoclinic, H — hexagonal $\text{GdO}_{1.5}$ -based solid solutions; Pyr — pyrochlore structure $\text{Gd}_2\text{Zr}_2\text{O}_7$ (with homogeneity ranges), AL — Al_2O_3 (corundum), GAM — monoclinic phase $\text{Gd}_2\text{Al}_4\text{O}_9$, GAP — perovskite structure GdAlO_3 , L-liquid.



In another example, the metallic system Mg–Al–Mn, it was shown that a quantitative description of the small joint solubility of Al and Mn in liquid Mg could be obtained only by re-modeling the pertinent binary Al–Mn solid phases [22]. In fact, in the temperature range of interest no experimental data are available for these Al–Mn binary phases, thus justifying the re-modeling based on ternary experimental data.

This general scheme is applicable to all ternary systems composed either of pure elements or components which are strictly stoichiometric (oxides, salts). In the case of non-elemental components, the implication is that all the limiting sub-systems may be considered as quasi-binary and the system should be considered as quasi-ternary. This requires that all tie-lines are located in the A_xO_y – $\text{A}'_{x'}\text{O}_{y'}$ – $\text{A}''_{x''}\text{O}_{y''}$ quasi-ternary system and that they do not cross this section of the true A – A' – A'' – O system.

More complex situations may be found when some components are not strictly stoichiometric, for example with oxide systems that are of interest to the cement industry or for nuclear power plant applications. In these two cases, iron oxides are very important components and largely non-stoichiometric both in the solid and liquid state. However, experimental information is only available for a given oxygen potential, either in reducing conditions (in the presence of metallic iron), or in oxidizing conditions (in air or at $p_{\text{O}_2} = 1 \text{ atm}$). Binary or ternary experimental phase

diagrams are presented as FeO-oxides (reducing conditions) or Fe₂O₃-oxides (oxidizing conditions) and even in some cases as Fe₃O₄-oxides, with the oxides being either CaO, SiO₂, UO₂ or ZrO₂. In each of these cases, the real dimension of the system is increased by one, and thus:

- any of the FeO/Fe₂O₃/Fe₃O₄-oxide isoplethal sections and the FeO–Fe₂O₃-oxide isothermal sections may be calculated only from the thermodynamic modeling of real ternary systems Fe–O–X, with X=Ca, Si, U, Zr for example,
- the FeO/ Fe₂O₃- oxide'- oxide" isothermal sections or liquidus projections may be calculated only from the thermodynamic modeling of real quaternary systems Fe–O–X–Y, with X,Y =Ca, Si, U, Zr for example.

In these situations, the use of simplified quasi-binary or quasi-ternary systems is not appropriate as the compositions of the phases may deviate from the stoichiometry.

2.2. Quality assurance in database development

In the following four sections we will highlight four different criteria to check the validity of individual thermodynamic descriptions. These will be discussed for binary systems for simplicity and because it is of the utmost importance for a multicomponent database to be built on sound and reliable binaries. These criteria are, thus, relevant for both the direct use of binary systems and also the construction of multicomponent databases. To this end we will address the following four questions relating to thermodynamic descriptions (or datasets): are they (i) correct? (ii) reasonable? (iii) accurate? and (iv) safe? A more detailed picture with the special relationship to a multicomponent Mg-alloy database is given elsewhere [23].

It should be noted that many of the errors discussed in this section are found in older assessments. Some of these errors were the result of an unfortunate combination of the then available, less sophisticated software and insufficient awareness that these problems may occur. In many cases, the original thermodynamic description has been corrected, although these corrections are frequently only available through communication with the authors. New generation software [24], [25] and [26], as well as the present paper, should help to improve the quality of assessments. Unrealistic phase boundaries produced as a result of using an inappropriate choice of model parameters have been already discussed by Okamoto [27]. His basic advice, trying to keep the thermodynamic model as simple as possible, was clearly demonstrated for a large number of binary systems. Of course, the power of the Calphad technique is having the ability to perform calculations involving a large number of components. This requires the creation of large databases for higher order systems; and this, in itself, can pose problems that can trap the unwary. These issues are addressed in this section.

2.2.1. Correctness of dataset

A dataset is considered to be correct if it produces the intended stable phase diagram and thermodynamic properties. Otherwise this thermodynamic description is wrong. Generally, a proper phase diagram calculation is the most stringent test that can be performed with a reasonable amount of effort.

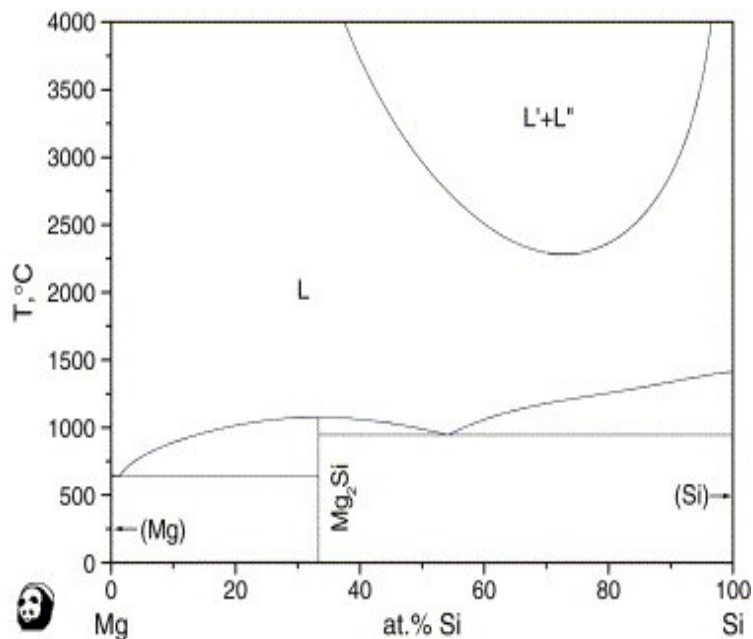
Some typical “troublemakers” in given datasets (or after assembly in a major database) are typographical errors in parameters or wrong/unclear reference states or molar basis ambiguities (per mol-formula/mol-atoms/sites). These are often easily removed after detection. More difficult to find are the following three cases, where inadvertently incorrect assessments have been

produced because the assessor was not aware of the true stable phase diagram calculated using that particular dataset. It is strongly recommended to calculate phase diagrams by using a number of different software packages. The following three artifacts are encountered most frequently when scrutinizing given datasets: (i) inverted miscibility gap, (ii) re-stabilization of solid phases at high temperature and (iii) inadvertent stability of ordered phases.

2.2.1.1. Inverted miscibility gap

It is often the case that, when using linearly temperature dependent interaction parameters for the liquid phase, an inverted liquid miscibility gap appears at unexpected temperatures. This is often overlooked by assessors, since not all software is capable of detecting miscibility gaps automatically. Many examples of the occurrence of inverted gaps along with detailed explanations have been shown by [24] and [25]. As an example, the Mg–Si dataset as assessed by [28], shows such an inverted miscibility gap at high temperature if the phase diagram is calculated with software that detects the gap automatically, see Fig. 2. Another erroneous Mg–Si example [29] and a corrected dataset for the Mg–Si system is given by [30]. Therefore, assessors should be aware of this problem, which is very common in the literature. To ensure that no such miscibility gap will appear, one could calculate the stability function, $\partial^2 G^{\text{Liquid}} / \partial x^2$, at various points in areas of interest and check that it is always positive. Another possibility is to use software with global Gibbs energy minimization algorithms that will automatically find the gap by searching for global instead of local minima of the Gibbs energy [25].

Fig. 2. Calculated phase diagram of the Mg–Si system using parameters from [28]. An unrealistic inverted liquid miscibility gap is produced, which is also observed from another parameter set [29] and eventually corrected in [30].



The reason for the occurrence of the inverted gap and why it cannot be accepted will be discussed

below. Let us assume that the liquid binary interaction parameter is described by the most popular linear temperature dependency, using a parameter in the form

$${}^0L^{\text{Liq}} = a + bT \quad (3)$$

for example, in a regular solution model. This means that the enthalpy of mixing and the excess entropy of mixing, related to the constant parameters a and b , respectively, will differ from zero even at infinite temperature. This is the basic problem. To assume that these quantities are constant is quite suitable in a *limited* temperature range, and often supported by experimental data.

Generally, a and b should have differing signs which means that the enthalpy and the excess entropy of mixing should have the same sign [31]. If both, enthalpy and entropy, are negative (i.e., $a < 0$ and $b > 0$) then the excess Gibbs energy at mid-composition grows infinitely positive with T . This results in an inverted miscibility gap with a lower critical temperature of

$$T_{c,\min} = a/(-b + 2R). \quad (4)$$

This is clearly unrealistic and is an artifact produced just by extrapolating the oversimplified temperature dependence, since we should consider that the *excess* mixing terms tend to zero with $T \rightarrow \infty$. This does not contradict the fact that real systems (e.g. organic) exist with a lower critical temperature and demixing occurs over some limited temperature range. In any case, at very high temperature the gap should again shrink with T and not widen following Eq. (3), as is the case in the identified examples [24], [25] and [30]. There are many more examples of this artifact in the published literature.

This behavior might be tolerated for practical reasons if $T_{c,\min}$ is much higher than the maximum temperature envisaged for the use of this dataset. Another limitation may be in the validity of the unary data at very high temperature. One should keep in mind, though, that even somewhat below $T_{c,\min}$ the chemical activities will become unrealistic functions of composition. Another point to consider is that combining such a dataset with refractory components or high melting phases will require very high values of $T_{c,\min}$. As a rule-of-thumb one might propose $T_{c,\min} > 4000 \text{ K}$ if the maximum temperature for using the dataset is 3000 K. The $-a/b$ ratio should be in the order of 3000 K for most systems, as suggested by [31] and [32], which imposes an additional constraint, as seen from Eq. (4).

Another possibility is to try to avoid the artificial miscibility gap completely, by bringing the liquid excess parameters to zero at high temperatures. Kaptay [31] suggested an exponential function of the form

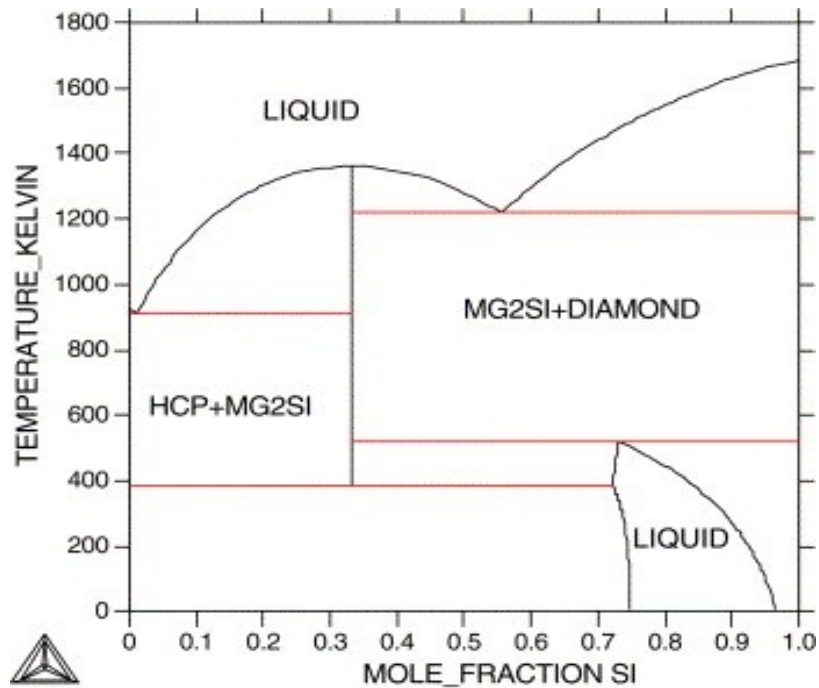
$${}^0L^{\text{Liq}} = h_0 \exp(-T/\tau_0). \quad (5)$$

Here h_0 and τ_0 are the two adjustable parameters, with τ_0 suggested to be, again, of the order of 3000 K. The reasoning proposed by Kaptay [31] is convincing since Eq. (5) satisfies all the necessary boundary conditions at high (and low) temperatures that are demanded. It is also true that over a limited temperature range, where actual experimental data may be provided, the exponential function does not visibly deviate from a straight line, as shown by Kaptay in a graph for the range $0.3 < T/\tau_0 < 0.4$. However, no Calphad type analysis was performed in that paper [31].

We have attempted to re-model the Mg–Si system using Eq. (5). This is a good test system since it contains just one stoichiometric intermediate phase, Mg_2Si , having a well defined Gibbs energy and so only the Gibbs energy of the liquid remains to be adjusted. In fact, the inverted gap is

avoided, as expected. However, for all the model parameter settings that came close to a proper description of at least the invariant phase equilibria in Fig. 2, another artifact at low temperature is observed. Because of the negative enthalpy of mixing in liquid Mg–Si alloys, one must have $h_0 < 0$, resulting in negative excess Gibbs energy. The exponential function, however, exaggerates this negative excess Gibbs energy at very low temperature, resulting in the re-stabilization of the liquid phase way below the solidus. One example of this artifact for some test values of the parameters is shown in Fig. 3.

Fig. 3. The calculated Mg–Si phase diagram using the exponential equations (6).



The figure shows an attempt to reproduce the stable phase diagram by just refitting the liquid description with two Redlich–Kister excess parameters with an exponential temperature dependence according to that model:

$$\theta_L^{\text{Mg,Si}} = h_0^{\text{Mg,Si}} \exp\left(-\frac{T}{\tau_0^{\text{Mg,Si}}}\right) \quad (6b)$$

$${}_1L^{\text{Mg,Si}} = h_1^{\text{Mg,Si}} \exp\left(-\frac{T}{\tau_1^{\text{Mg,Si}}}\right).$$

The optimized values of the 4 coefficients resulting from using only the invariant phase equilibria as experimental information was $h_0 = -95\,358\text{ J/mol}$, $\tau_0 = 1303.8\text{ K}$, $h_1 = 15\,442\,793\text{ J/mol}$ and $\tau_1 = 120.6146\text{ K}$. In the previous assessments [30] even three Redlich–Kister parameters were used in order to also describe the experimental thermodynamic data. The attempt based on Eqs. (6) removed the inverted miscibility gap but instead the liquid became stable at low temperature, see Fig. 3. This artifact may be avoided by keeping track of the values of h and τ or by adding extra experimental information to prevent the liquid from becoming stable below some limit (e.g., 100 K), but it shows that the exponential model cannot be used without care.

Therefore, the basic idea of Eq. (5) is good and clearly superior to the popular linear equation (3) and, in fact, solves the problem associated with high temperatures, but unfortunately may induce a new problem at low temperature.

The search for an improved function could not be completed within the scope of the present study. However, the following guidelines are given. The function should tend to zero, as in the case of Eq. (5), at high temperature without an excessive increase at low temperature. For instance, the introduction of a multiplier function may be suggested, such as

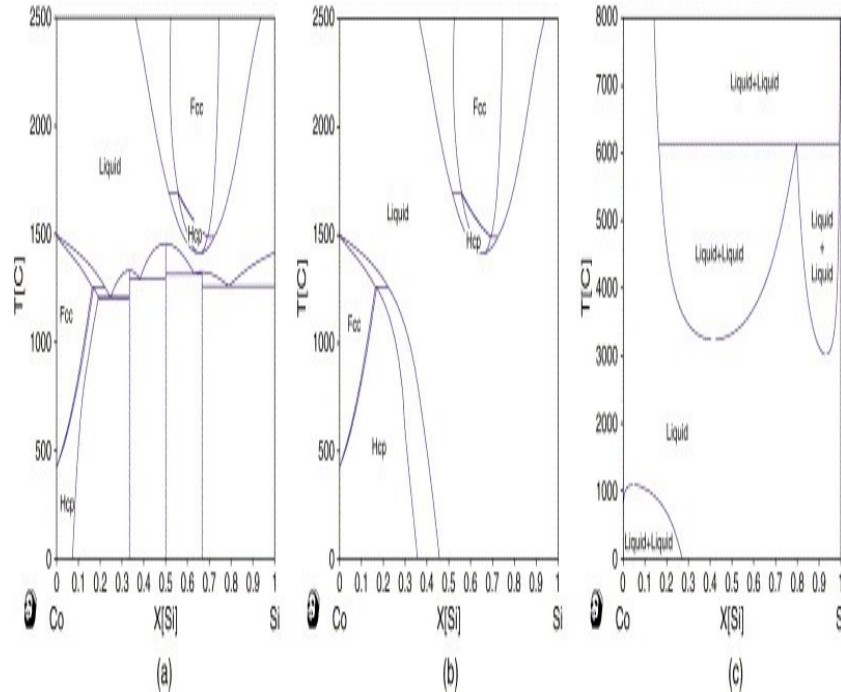
$${}_0L^{\text{Liq}} = (a + bT)f(T). \quad (7)$$

Here $f(T)$ should have a “smooth” S-shape behavior, while still continuous (e.g., an error function or hyperbolic tangent). In addition it should have an analytical derivative and also be computationally efficient. The latter may rule out the error function. In any subsequent study to find a suitable temperature dependency of ${}_0L^{\text{Liq}}$ it is strongly recommended to test the function with a number of complete Calphad assessments.

2.2.1.2. Re-stabilization of solid phases at high temperature

There exist other features that are frequently overlooked by assessors. For instance, solid phases appear outside their expected stability region, without any physical justification. For example, using the assessed parameters of Choi [33] for the Co–Si system, a re-stabilization of the hcp and fcc solid solution phases slightly above the stable liquidus line and up to very high temperature was found if the calculation is carried out with software that detects the truly stable phase diagram automatically, see Fig. 4(a).

Fig. 4. The Co–Si phase diagram calculated with the parameters from [33]: (a) stable phase diagram; the inadvertent re-stabilization of solid phases at high temperature is noted; the low temperature part of the liquidus lines corresponds to experimental data; (b) metastable diagram, allowing hcp, fcc and liquid only; (c) metastable diagram, allowing liquid phase only.



This problem cannot be easily avoided by simply plotting and reviewing the (liquid+solid) metastable extrapolations for the whole composition range as demonstrated in Fig. 4(b). The L+hcp/fcc equilibria are separated in a low temperature part (real) and a high temperature part (artifact). Even in such a metastable L+hcp/fcc phase diagram calculation, the isolated high temperature part could be found only if the assessor suspects its occurrence and chooses starting points for the calculation that lie in that range or, alternatively, as done for Fig. 4, using software that calculates all equilibria automatically [24]. In the Co–Si example, the re-stabilization of solid phases is not only due to a peculiar setting of parameters for the hcp and fcc phases but also to the strange behavior of the liquid phase showing four different miscibility gaps, all of them revealed by calculating the metastable phase diagram of the liquid phase, Fig. 4(c). Even though the particular inverted twin gap occurs only above around 3000 °C, it shows an impact on the low thermodynamic stability of liquid in the range of the artifact in Fig. 4(a). Most of these liquid gaps remain metastable with respect to the liquid+solid equilibria; a stable equilibrium $L'+L''=fcc$ is revealed only by calculating Fig. 4(a) (or Fig. 4(b)) to much higher temperatures (13 300 °C). Even though the basic artifact is clearly demonstrated by Fig. 4(a), the information of the metastable liquid phase diagram (Fig. 4(c)) may be useful for a revision of the thermodynamic parameters of this system.

2.2.1.3. Inadvertent stability of ordered phases

Low temperature phases, usually ordered, may not be detected automatically by some software, unless the initial condition for the equilibrium calculation is already close to its stable temperature, composition and site occupancies. This problem requires precise starting guesses and is harder to detect than the previous cases, so the use of a global minimization algorithm is the most straightforward way to check. As an example, using the parameter set given in [34] for the Al–Nb system, the calculation using such software revealed the artificial stability of a B2_BCC ordered phase below 800 K around 55 at.% Nb¹ [25]. In this example the B2_BCC phase does not occur in real Al–Nb alloys under any conditions but it is introduced in the parameter set from a multicomponent system Al–Nb–X.

As another example, in Al–Mn alloys the ordered B2_BCC phase is stable at around 50 at.% Mn and from ≈ 850 to 975 °C. The inadvertent and artificial reappearance of this ordered B2_BCC phase below 152 °C and around 32 at.% Mn was detected [22] in a published parameter set. Using the Pandat² software [24] it was possible to avoid this artifact in a reassessment of the Al–Mn system that was also required for other reasons [22].

2.2.2. Reasonability of dataset

There are some simple ways to check if the thermodynamic description is realistic.

There are also some examples of phase diagrams that appear reasonable, but on closer inspection exhibit unrealistic thermodynamic features.

Checking the absolute entropies of all solid phases at 298 K, S_{298}° , provides a very stringent test. For example, it was shown by [35] that in an earlier assessment of the Al–B system the calculated phase diagram looked reasonable even though the value of $S_{298}^{\circ}(\text{AlB}_2)$ was negative (!), $-1.9 \text{ J}/(\text{mol K})$.³ A plot of S_{298}° versus x_B demonstrates that the reassessed value of $S_{298}^{\circ}(\text{AlB}_2) = +14.3 \text{ J}/(\text{mol K})$ is also close to a straight line connecting the entropies of the stable elements [35]. This is an easy way to check if the entropies of formation are reasonable and is, therefore, recommended as a standard test.

Another recommended test is to plot the calculated phase diagram, not only with the composition as abscissa ($T - x_B$), but also with the chemical potential as abscissa ($T - \mu_B$). The slope of the two-phase lines in the latter plot indicates clearly if an inadvertent phase decomposition may occur just outside the calculated temperature range.

In addition, a plot of the enthalpies of formation at 298 K, $\Delta^{\circ}H_{298}$ versus x_B is recommended to detect peculiarities such as a non-convex shape. If there are no experimental (or possibly ab initio) values available to compare with, such a plot may not be published but is still useful as a check. A comparison to estimated values, such as the Miedema values [36] or guidelines given by Kubaschewski et al. [37] should always be considered.

One may argue that an experienced assessor could also judge the reasonability from a careful look at the numerical values of the thermodynamic parameters. On the one hand this is true, and a critical judgment of numerical parameter values is essential especially if using parameter optimization software. On the other hand there are examples, as mentioned above, where unrealistic parameters slipped through in publications of experienced assessors. It is thus highly recommended to routinely perform the graphical tests, S_{298}° versus x_B , $T - \mu_B$, and $\Delta^{\circ}H_{298}$ versus x_B .

2.2.3. Accuracy of dataset

A comparison between the calculated phase diagram and reliable experimental/ab initio data will reveal the level of accuracy of the thermodynamic description. Usually, a figure showing the calculated phase diagram/thermodynamic properties is sufficient. It is important, however, to check, if the deviations have a Gaussian distribution over the whole range of composition and/or temperatures. For that purpose, it is sometimes necessary to look at the difference between experimental/ab initio and calculated values.

In most cases, the accuracy of a thermodynamic assessment is directly related to the internal or mutual consistency of experimental datasets. One may be also afraid to use additional interaction parameters in the description at the expense of the accuracy. Finally, an inaccurate assessment may originate from inappropriate rounding-off of parameters. As a rule-of-thumb, rounding-off the Gibbs energy terms to 0.1 J/mol at 1000 K is recommended.

Since any assessment is always subject to further improvement, the assessor or user has to decide if the accuracy is good enough for publication or application, respectively.

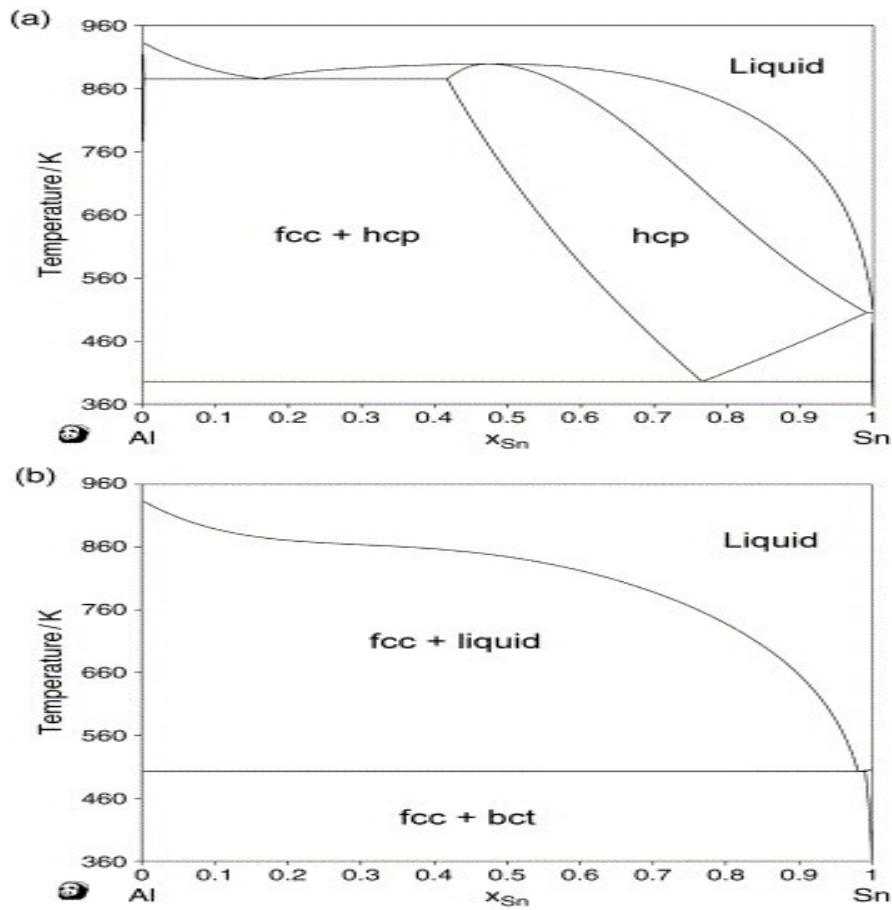
2.2.4. Safety of dataset

The first step in the development of a multicomponent thermodynamic database is a compilation of all binary, ternary, and higher order assessments which cover the elements of interest (see also Section 3). If a thermodynamic description has been proven to be correct, reasonable, and accurate it still does not mean that it is safe to use for calculations relating to multicomponent systems without further checking. Usually, database managers face problems of three different kinds:

- (1) Missing assessments of subsystems
- (2) Automatic interpolation between unstable end-members
- (3) Close proximity of stable and metastable phase boundaries.

The first two problems are actually consequences of the fact that some software assumes zero for a particular parameter if it is missing in the database. If an assessment of a subsystem is missing completely, the database should not be used for calculations in the corresponding composition ranges. This must be clearly stated in the documentation to avoid producing wrong results (see also 3.1.3). The problem becomes more severe if two or more unstable end-members of a solution phase come together for a particular combination of elements. For example, a database for lead-free solders may contain elements such as Ag, Al, Mg, Sn, and Zn. When calculating the binary Al–Sn phase diagram with a database created by a compilation of all binary assessments [34], one may observe that the hcp phase exists in the region of <40 at.% Sn (Fig. 5(a)). Both Al and Sn are unstable in the hcp structure, so there is no need to consider this hcp phase in the binary Al–Sn at all. The hcp phase is simply introduced as an end-member phase in the multicomponent database. Such artifacts can be avoided by assigning a large positive value to the regular interaction parameter of the metastable phase (Fig. 5(b)).

Fig. 5. (a) The Al–Sn binary phase diagram calculated using the COST 507 database for light metal alloys [34]; (b) the same diagram after introduction of the regular interaction parameter ${}^0L(\text{hcp, Al, Sn}) = +100000 \text{ J/mol}$.



The close proximity of stable and metastable phase boundaries is not obvious and often difficult to avoid. Let us consider the Cu–Sn system as an example. Fig. 6(a) shows the metastable phase boundaries calculated assuming that only the liquid and fcc phases are present in this binary system. In Fig. 6(b), these curves are shown as dashed lines superimposed on the equilibrium phase diagram, which has been calculated with the same set of parameters [38]. It is easy to see that between 60 at.% and 80 at.% Sn, the metastable fcc and stable CuSn_3 liquidus lines are very close to each other. As a consequence, the fcc phase may unexpectedly appear in a higher order system in the composition range far away from its homogeneity range, just owing to an increase in the configurational entropy. Such a situation is illustrated in Fig. 7, where the fcc phase becomes stable again in the Sn-rich part of the Cu–Sn–Ni phase diagram. This thermodynamic description needs to be corrected.

Fig. 6. Metastable fcc+liquid phase boundaries in the Cu–Sn system (a) without and (b) with the equilibrium phase diagram superimposed.

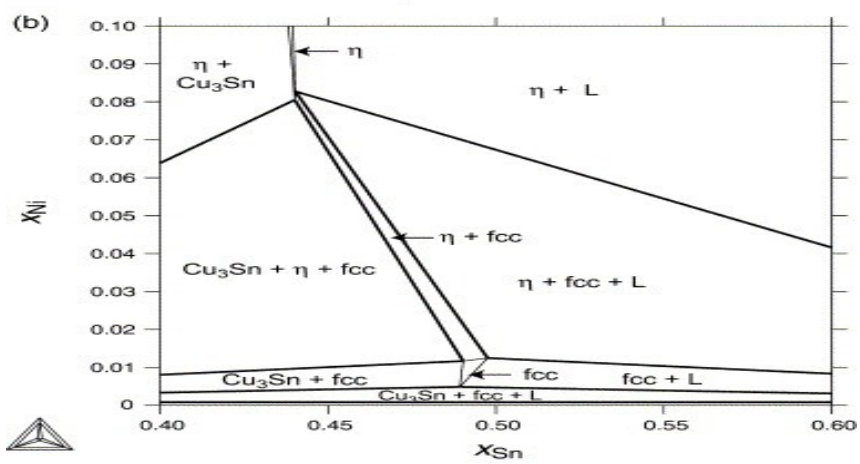
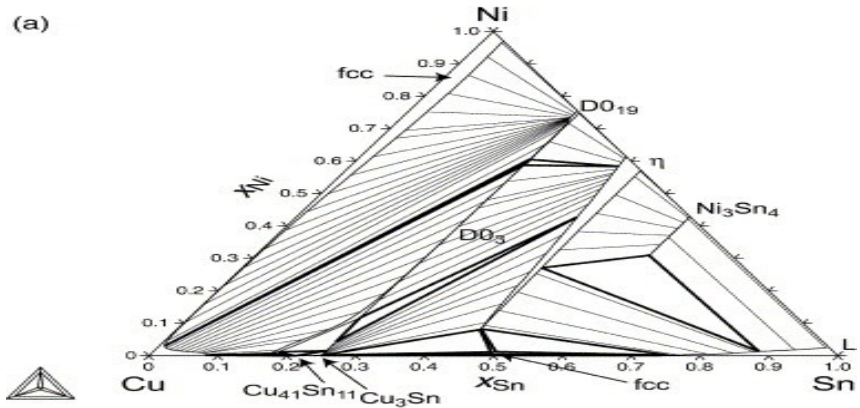
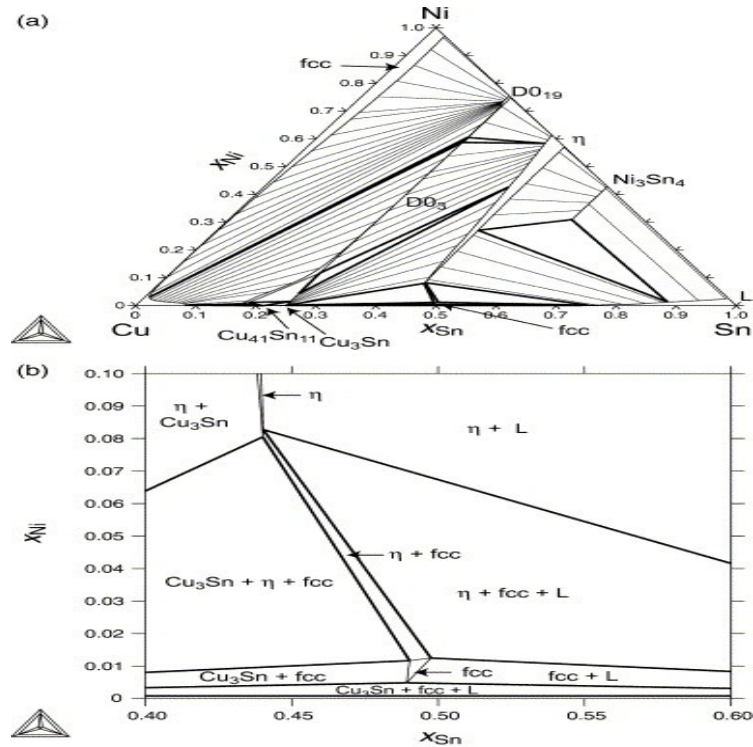


Fig. 7. Calculated isothermal section of the Cu–Sn–Ni phase diagram at 773 K. (a) Entire composition range, (b) detail showing the artificial appearance of the fcc phase in Sn-rich alloys near the Cu–Sn binary edge.

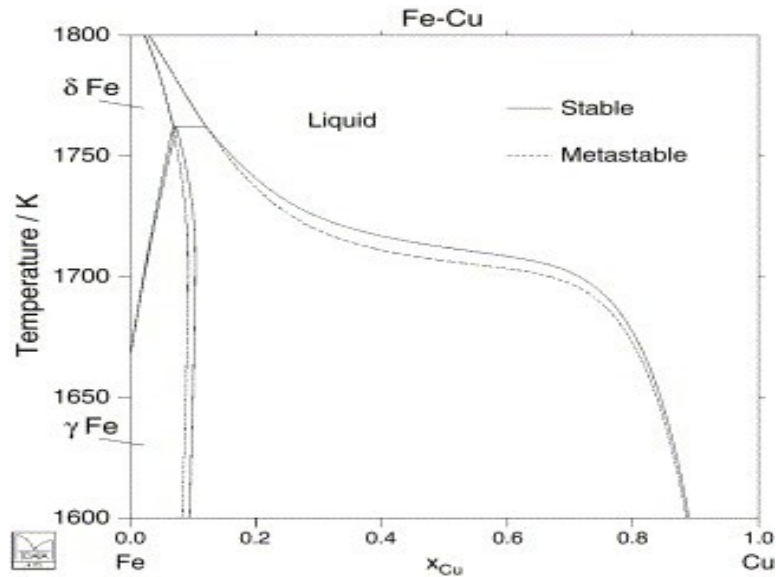


Suspending the interfering phase in calculations is not always possible because it can be stable in some subsystems. Therefore, it is important to calculate stable and metastable phase boundaries in every subsystem and to ensure that they are clearly separated before combining the corresponding thermodynamic descriptions in a multicomponent database. A possible solution is to give a higher value for the interaction parameters for the metastable phase in the binary system, so that it will be destabilized. One may also need to revise the lattice stability or Gibbs energy of a particular end-member.

However, it may sometimes be difficult to judge how large a gap between stable and metastable phase boundaries should actually be. The best practice is to rely upon experimental or ab initio data for the metastable phases and/or experimental data for the metastable phase equilibria. In some cases, the proximity of the stable and metastable phase boundaries is well-justified thermodynamically, and thus, trying to separate them would be incorrect. A good example is the Cu–Fe system (Fig. 8). This figure shows the Cu–Fe phase diagram calculated for temperatures between 1600 and 1800 K using data from the SGTE solution database [39]. The solid lines represent equilibrium phase boundaries, and the δ -Fe and γ -Fe single phase fields appear as shown. The dashed lines are the metastable phase boundaries which result when the γ -Fe phase is removed from the calculation. From the equilibrium phase diagram, crystallization of γ -Fe (fcc) is expected for alloys with $x_{\text{Cu}} > 0.15$. However, rapid solidification often results in the precipitation of δ -Fe (bcc) from the melt even in Cu-rich alloys [40] and [41]. Thus, the proximity of the metastable bcc + liquid field to the stable liquidus line is a reality in contrast to the Cu–Sn

example discussed above.

Fig. 8. Stable (fcc+liquid) and metastable extrapolations of (bcc + liquid) phase boundaries in the Fe–Cu binary system calculated using the thermodynamic description taken from SGTE solution database [39].



2.3. Dissemination of assessment results

In the section on good assessment practice (2.1) we pointed out the importance of proper documentation of a thermodynamic assessment. Proper documentation should include a description of the optimization process and a summary of the experimental data and assigned experimental errors that were used in the assessment. This information should also be included in the publication of the assessment. The publication should also identify whether further experimental work is needed. Model parameters that were derived in the assessment and those that were taken from the literature should be clearly identified. For complex systems or higher order systems where the list of all model parameters can be quite extensive, it may be advisable to list only the model parameters that were derived in the assessment and give literature citations for the other parameters.

Occasionally results from an assessment are published in the literature without providing the model parameters that were used to obtain the calculated diagrams. This practice severely limits the usefulness of the results for the reader, since it is impossible to judge the quality of the assessment and an assessment without the derived thermodynamic parameters provides little new information on the system. In addition, the thermodynamic description is not available for additional calculations. Therefore, we recommend journal editors to reject manuscripts that fail to list the parameters that were derived in the presented work.

It is obvious that the published description must be free from errors to enable the reader to reproduce the results of a calculated system. Even a minor typographical error in the numerical values, such as an omitted minus sign, a digit or a decimal place, can make it impossible to reproduce the calculated diagrams. In order to minimize the occurrence of typographical errors, it

is desirable for a data file containing the description be submitted in electronic form for the peer review.

3. Database design

When designing and assembling a database, it is of great importance that the thermodynamic data used are of the highest quality. At each stage of the database development a certain amount of testing is required.

It is good practice to start by collecting a complete set of component unary Gibbs energy expressions that will cover the scope of the database for the particular application for which it will be used. Following a “bottom up” approach, the construction of the database is continued by adding thermodynamic expressions from binary assessments. At this point, it is necessary to ensure that there is consistency in the phase names and models used. For example, it is desirable that all occurrences of the same type of intermetallic phase should use the same type of model with the same number of sublattices and stoichiometry. This would allow, in principle, for mixing of the different binary phases in higher order systems. If there are mixtures of descriptions for the same type of phase it is necessary to reassess the appropriate systems to gain consistency. However, there are cases where it is desirable that similar phases should not have the same name; for example, where it is known that mixing between the phases is not possible. A second check is to make sure that the chosen component unary expressions are consistent with the binary assessments compiled for the database. Each binary system must be checked to ensure that the correct phase diagram and thermodynamic properties can be reproduced. Again, if there are any discrepancies, reassessment of the appropriate binaries is required. This process is repeated for any ternary assessments or even quaternary information that may be added to the database.

Testing is an important part of the database preparation process and it is often useful to use a number of different software packages for this. Different software packages have different strengths and this can be extremely useful in database design. Also, if it is intended that the database will be used by different users who may have different software, it is important that there are no problems in transporting the database between the different packages.

3.1. Database types

Generally, two types of database can be distinguished.

3.1.1. End-user database

An end-user database is considered to be a complete stand-alone database. This is often prepared for a particular application but can also be general in nature. It should not require any model changes or phase selection in order to make a calculation. Only the conditions of the equilibrium (composition, temperature and pressure) need to be entered into the computation software. It can be used directly by a non-specialist user for applications for which it was designed.

3.1.2. Compilation database

A compilation database may actually contain many separate databases that have been put together into a single database. There is a danger however that the same phase may appear more than once with different thermodynamic descriptions, for example as a stoichiometric phase and as a phase with a homogeneity range. These databases should be used with a high degree of caution and it is incumbent on the user to take care in selecting the appropriate set of phases for each calculation in order to prevent spurious results.

3.1.3. Documentation

The database should be accompanied by appropriate documentation as text within the database, and/or an accompanying electronic text file or hard copy. Indication of the validity of the database in terms of temperature and composition range, and also a list of phases and the assessed sub-systems (binary, ternary, ...) will provide the user with important information to allow the user to perform reliable calculations. Useful calculations outside the validity range are possible, but these should be treated with a degree of caution. It is also useful to indicate the sources of the data, for example as a reference to a particular article where assessed data can be found. Some software can reveal this information, if it is stored in the database in the appropriate format, at the time when the data are retrieved from the database. It may be useful to give some sort of indication as to the quality of the data from each source, by a grading system. For example, a system denoted as "A" would indicate data are considered to be of the highest quality (see Section 2.2). "B" could denote a system, which does not meet all quality criteria, but the agreement with the experimental data is satisfactory. A system denoted "C" could indicate a system which needs improvement owing to insufficient experimental information. "D" could refer to a system which has been estimated. In any case, the grading scheme should be defined within the documentation.

Information relating to features such as miscibility gaps should be included in the documentation, and flags and other such features should be added to the database to allow automatic searching for stable miscibility gaps by the computation software, if this feature is available.

3.2. Phase designation

There is no generally accepted method of assigning names to phases. Typically, in binary systems, phases are named with Greek letters like α , β , γ , etc. from low temperature at the left hand side of the phase diagram to the right hand side. Stoichiometric compounds are often named after their composition like Al_3Ni . For solution phases, one sometimes finds (Al) for a solution phase consisting mainly of Al, and in steels, phase names like ferrite and austenite are generally used. However, in a database, a phase may exist over a large composition range and including several pure elements. All phases that may form a continuous solution and are described with a single Gibbs energy function must be treated as a single phase in the database, and it simplifies things if the name is independent of the composition of the phase.

The phase name should also fulfill some minimal criteria of being understandable by the user of the database and provide some minimum of information about the phase, especially since this name may appear in the interactive labeling of phase diagrams. It must also be readable by different software and thus Greek letters as well as super- and subscripts should be avoided. The name should preferably consist of just letters and digits and a few special characters like the underscore or the hyphen. Below, the use of a slash "/" in phase names is also recommended.

The *GAS* phase is no problem, as long as it is ideal, but "real gases" may need some separate names. The liquid is much more problematic as there are usually several different incompatible models used for different types of liquids; such as oxides, mattes, metallic, molten salts and aqueous. It is possible to treat the metallic liquid as distinct from the oxide liquid if they are separated by a miscibility gap and thus use different names like *LIQUID-METAL* or *SLAG*. But with improved modeling, it may be possible to describe different composition ranges with the same model and thus use the name *LIQUID* for this phase. The amorphous phase rarely occurs in databases and little is known about the possibility of it forming continuous solutions, so such phases may be simply named *AMORPHOUS*, possibly with some additional identification like *AMORPHOUS-SIO*. However, it must be well specified if a glass (or frozen liquid, FL) is treated with a separate Gibbs energy equation from the liquid (or supercooled liquid, SL) as detailed, for example, in the case of non-crystalline SiO_2 [42].

For the crystalline solid phases, there are more options for the name. Since the crystalline lattice is the most important feature, it is recommended that one uses the simplest identification of the lattice for the name. Thus, the stable solid phase of Cr, Mo, low temperature Fe, etc. should be called *BCC*. For additional specification, one may use *BCC_A2* but the “Strukturbericht” [43] designation A2 is not really necessary. Note that *BCC* is used as the name of the phase, not the lattice. However, not all crystal structures that exist, even for pure elements, have unique lattices. For example, pure Ga and pure U have different types of structures in the same orthorhombic lattice and these phases then need an additional specification, for example the Strukturbericht designation. Other pure elements, such as B and several modifications of U and Pu, have no simple lattice names. The Strukturbericht designation, consisting of one letter followed by a number and possible subscripts, would have been a very natural choice for phase identification, but for the last 50 years there has been no authority who assigns Strukturbericht designations, and many odd “Strukturbericht-like” designations are now used for phases that have been discovered in recent years. It would be beneficial if this problem was resolved. A current compilation is found on the Naval Research Laboratory Web Site, <http://cst-www.nrl.navy.mil/lattice/struk/>.

The SGTE (Scientific Group Thermodata Europe, <http://www.sgte.org>) has a large solution database and the phase names used have been generally accepted in other databases. These names are based on the lattice and additionally use the Strukturbericht designation for specification. Some intermetallic phases have retained their Greek names, but written with Latin letters, like sigma and mu, as the same Greek letters have been used for the same phase in different systems. The current recommendation follows this convention but puts more emphasis on the Strukturbericht designation, as this is of greater help in identifying phases from different databases or assessments that have the same structure and therefore should be treated as the same phase.

One must also consider that there are phases that may have the same lattice or even the same Strukturbericht designation but that will never form a continuous solution; for example NaCl and TiC. In these cases, one should not use the same name for these phases, but still retain the structure information, like B1_HALITE and B1_CARBIDE. However, for the TiC phase, there is a significant amount of vacancies in the carbon sublattice, and if all of the carbon is removed we have an fcc structure and the Strukturbericht designation is actually A1. So, a more informative phase name may be B1_FCC. These “families” of structures will be discussed in more detail below.

For phases that have a completely unknown structure one should start with the elements that dissolve in the phase, followed with some identification like *ALCU_THETA*. One must never use a name just like *ALPHA* as there are many phases in different systems called *ALPHA* but with completely different structures. The space group and other crystallographic information are not really interesting to add, because two phases with the same space group can have completely different structures. If the Strukturbericht designation is known, the recommendation is to use that as the first part of the phase name, except for the simple structures like fcc, bcc, hcp, diamond etc. When the Strukturbericht designation has a subscript like in D0₁₉, this can be separated from the first part with a slash; like in D0/19.

In [Table 1](#), the aim is to use a single phase name for phases that can form a continuous solution from one composition to another, which normally implies that they have the same structure. Phases with the same structure that will never form a continuous solution, like NaCl and TiC or Fe₃C and Al₃Ni, should have different names even if they have the same Strukturbericht designation.

Table 1.

Recommended phase names for some crystalline phases

Phase name	Strukturbericht designation	Stable for elements or composition	Notes
FCC	A1	Ni, Cu, Ag ...	
BCC	A2	Cr, Mo, V ...	
HCP	A3	Mg, Zr, Co, Cd, ...	
A12_CBCC	A12	Mn	Complex BCC
A15_ZR4SN	A15	Zr ₄ Sn	
B1_HALITE	B1	NaCl ...	Salt
B1_OXIDE	B1	CaO, FeO	Oxide
B1_FCC	B1	TiC, ...	Interstitial FCC
B2_BCC	B2	AlNi, FeTi, ...	Ordered BCC
B3_ZINCBLLENDE	B3	GaAs, ...	
C1_FLUORITE	C1	CaF ₂ , ZrO ₂ , ...	
C14_LAVES	C14	Co ₂ Ta	
D0/11_CEMENTITE	D0 ₁₁	Fe ₃ C	
D0/11_AL3NI	D0 ₁₁	Al ₃ Ni	
D0/19_HCP	D0 ₁₉	Ti ₃ Al, ...	Ordered HCP
D10/1_M7C3	D10 ₁	Cr ₇ C ₃	Carbide
D5/1_CORUNDUM	D5 ₁	Al ₂ O ₃ , Fe ₂ O ₃ , ...	Oxide
D8/5_MU	D8 ₅	Co ₇ Nb ₂ , ...	μ phase
D8/B_SIGMA	D8 _b	Fe–Cr, ...	σ phase
H1/L_SPINEL	H1 _L	Al ₂ MgO ₄ , Fe ₃ O ₄ , ...	Oxide
L1/0/2_FCC	L1 ₀ +L1 ₂	TiAl, Ni ₃ Al, ...	Ordered FCC
ALCU_THETA	?	Al ₂ Cu	θ phase in Al–Cu
TLSE_LOWT	?	TlSe	Low <i>T</i> form of TlSe
SITi3	?	SiTi ₃	

[See text for explanation.]

In the thermodynamic modeling of a phase, it is important that phases that can be described with the same Gibbs energy function are given the same name. Thus, ordered phases like Ni₃Al with the L1₂ structure should have the same name as the disordered A1 structure. In [Table 1](#), the name L1/0/2_FCC is suggested because there is also an ordered L1₀ phase based on the fcc structure. In databases without these ordered structures, the simpler name FCC can be used. If one has ordered

fcc phases including carbon, the naming may become really complicated, and in the end-user database, one must make an appropriate choice depending on the customer, but in the compilation database as much structural information as possible should be kept. There are several such “families” of structures like D0₃, B2 and A2 based on the bcc structure, and D0₁₉, B19 and A3 based on the hcp structure. All of these phases may then have an interstitial sublattice, and possible ordering also on the interstitial sublattice, like the HCP phase in the Zr–O system. The names of these phases should reflect, as much as possible, how many of these structures the model for the Gibbs energy can handle, without becoming incomprehensible.

4. Software facilities for thermodynamic calculations

There are several software packages available for thermodynamic and phase diagram calculations involving binary, ternary or higher order systems. Most of them are distributed commercially; therefore they require license agreements for their utilization. Each software package has different features and capabilities, such as an optimizer to perform assessments, different phase models or a graphical user interface. The list below is a compilation of different capabilities found in most software for thermodynamic and phase diagram calculations:

- Maximum number of components
- Local and/or global minimization algorithm
- Comprehensive choice of setting conditions
- Types of calculations:
 - Point calculation
 - Line calculation
 - Two-dimensional section
 - Liquidus projection
 - Scheil solidification simulation
- Phase models:
 - Redlich–Kister (substitutional solution)
 - Gas (molecules)
 - Stoichiometric compounds
 - CEF (Compound Energy Formalism)
 - Associate Solution (not charged)
 - Ionic liquid
 - Quasi-chemical model

- CSA (Cluster Site Approximation)
- Others (aqueous solution, cell models, etc.)
- Optimizer
- Number of parameters for simultaneous optimization.

For the selection of a particular package, a user should consider which points are most important to his/her particular interest, because some of the functionalities listed above will not be present in all packages.

A selection of the most popular packages is listed in [Table 2](#), together with web links to the software providers. A comprehensive summary of thermodynamic calculation software was published in a special issue of the CALPHAD journal vol. 26, iss. 2 (2002) pp. 141–312, so that [Table 2](#) also contains references to that issue (where applicable). The preface to that edition also contains a general introduction with a brief description of the software packages included in the special issue.

Table 2.

Selected software facilities for thermodynamic and phase diagram calculations

FactSage [44]	http://www.factsage.com
Lukas Programs [11] and [16]	Non-commercial software package by Hans Leo Lukas, Max Planck Institute for Metals Research, Stuttgart, Germany.
MTDATA [45]	http://www.npl.co.uk/mtdata
Pandat [46]	http://www.computherm.com
Thermo-Calc [47]	http://www.thermocalc.com
Thermosuited [48]	http://thermodata.free.fr
WinPhaD	http://www.computherm.com

5. Software facilities and databases for diffusion

Thermodynamic information is crucial for the simulation of many materials processes, such as diffusion. Most diffusion software packages calculate only diffusion processes for specific composition–temperature regimes that are defined by the experimental data that are used as input. The diffusion simulation package DICTRA [47] uses an approach for diffusion data that is similar to the Calphad approach for describing the thermodynamics of phases and, therefore, has the ability to extrapolate the diffusion descriptions beyond the original composition–temperature regime. Because of the similarity in the approaches, the general rules for developing thermodynamic descriptions, quality assurance and database design apply also to diffusion descriptions, i.e. the activation energy and the frequency factor, which define the mobilities of the diffusing species. The diffusion coefficients are calculated from the mobilities and thermodynamic factors. The latter are obtained from phase equilibria calculations using a thermodynamic database.

As with thermodynamic descriptions, the properties of the pure elements must be well defined to enable the assembly of a diffusion database for higher order systems. Unfortunately, a compilation of diffusion descriptions for the pure elements similar to that given by Dinsdale [11] for thermodynamic functions is currently not available.

The mobility functions are assessed using available experimental tracer, intrinsic, or chemical diffusion coefficients. Only the tracer diffusion coefficients are independent of the thermodynamic description. Thus, unless the mobility functions are assessed using only tracer diffusion coefficients, the diffusion mobility assessment will be dependent on the thermodynamic database used to obtain the thermodynamic factors. However, Campbell et al. [49] showed that the dependence on a specific thermodynamic database is insignificant if the quality of the thermodynamic descriptions is high.

6. Conclusion

We have shown that great care needs to be taken in the assessment of thermodynamic descriptions of binary and ternary systems, as well as in the construction of databases for higher order systems, and that adequate documentation is imperative. Because the thermodynamic description of a system is the result of significant effort, it is crucial to avoid duplication of work as much as possible. Therefore, the first step in developing a new description of a system should be a thorough survey of the literature to learn of existing descriptions. If one or more descriptions are found they must be critically examined using the criteria presented in this article and a new assessment should only be performed if a significant improvement over the best available description can be achieved.

It is obvious that checking the agreement between calculated and measured properties should be part of the assessment process. It should also become general practice that the thermodynamic description is subjected to quality assurance criteria during the assessment process, i.e., correctness and soundness of the dataset. Although continuing development of software for thermodynamic assessments and calculations will make this task easier, it will not absolve the researcher from scrutinizing the thermodynamic description prior to publication. The same scrutiny must be applied to the thermodynamic description of a system if it is being considered for implementation into a database for higher order systems. Although this may appear trivial at first glance, the selection of proper phase designations is a critical step in the construction of a database for higher order systems. Proper phase designations avoid not only ambiguities but also help to guide the end-user in the calculation of other system properties, such as metastable phase equilibria. Since the phase designation is only an abbreviated description of the phase, complete details must be provided in the database documentation.

Throughout this article, the importance of proper documentation has been emphasized. Proper documentation is imperative for the publication of the results and should accompany any electronic dataset. We strongly recommend that the publication of a thermodynamic assessment include the derived parameters.

We hope that this article will serve researchers as a guide for performing a thermodynamic assessment of a system and the development of databases for higher order systems, as well as provide useful information for reviewers and editors of scientific publications.

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