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Some guidelines for thermodynamic optimisation of phase diagrams

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Abstract

Thermodynamic optimisation of phase diagrams is a procedure that requires considerable experience and skill. The purpose of this article is to furnish certain guidelines that might facilitate the work and improve the quality of the thermodynamic optimisation of phase diagrams using the Calphad method. Some particulars regarding experimental data, Gibbs energy models, constraints on model parameters, and performing the optimisation are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phase diagrams can be calculated from Gibbs energy functions of phases [1]. The required Gibbs energy functions (thermodynamic descriptions) are usually obtained by a computer-assisted statistical procedure, using experimental thermochemical and constitutional data as input. Therefore, it is correct to note that optimising phase diagrams amounts to optimising of Gibbs energy functions. The generation and application of thermodynamic descriptions constitute the central theme of the so-called 'Calphad' [2] (an acronym for CALculation of PHAse Diagrams by computer coupling of phase diagrams and thermochemistry) method. In this method, each phase of the system under consideration is described using a Gibbs energy model. The model parameters are estimated by the weighted nonlinear least-square optimisation of thermochemical and constitutional data. Fig. 1 is a flowchart of the Calphad method. There are computer programs available for performing the Calphad tasks, e.g. *Thermo-Calc* [3], Lukas program [4], *ChemSage* [5], etc. which have modules to perform thermodynamic optimisation of phase diagrams. In order to produce a good thermodynamic description of a system using these programs, a great deal of expertise is required. The intention of this article is to provide some guidelines that may help the user in producing good quality thermodynamic descriptions.

2. Experimental data

The first step of the thermodynamic optimisation of a phase diagram is collecting and categorising experimental information. In principle any kind of experimental datum that is explicitly or implicitly linked to Gibbs energy can be used as input for the optimisation. One typically looks for constitutional and thermochemical data. All constitutional and thermochemical data must be extracted as numbers, even if only a graph is reported. Crystallographic information is also valuable, since it is useful in the Gibbs energy modelling. Although review articles serve as excellent sources of data, one should always consult the primary sources.

The second step involves the critical evaluation of the collected data, which is essentially eliminating bad and contradictory data. At this stage effort should be made to identify and exclude unreliable data. Critical evaluation requires considerable expertise and some familiarity with different experimental techniques. It is important that one must make a record of details such as technique used, phases present, purity of the sample, experimental conditions, quantity measured and its accuracy, etc. It is also useful to make graphical comparisons wherever possible. Frequently, difficulties faced during the least-square optimisation are due to poorly evaluated experimental data, and may indicate that the input contains contradicting or theoretically unacceptable data.

One of the main difficulties in the computerised thermodynamic optimisation of phase diagrams is that start values must be supplied for all model parameters that are opti-

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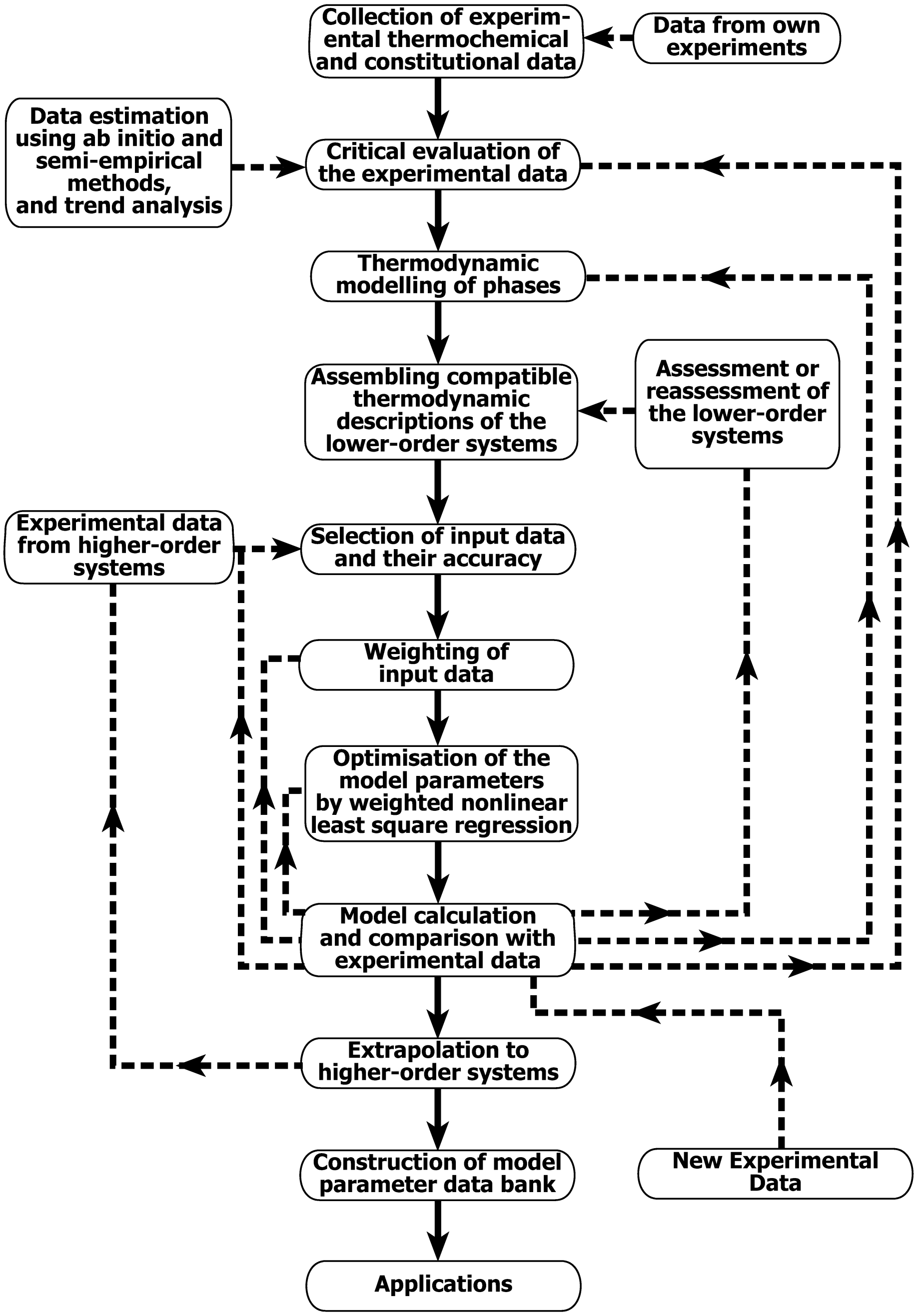

Fig. 1. Flowchart of the Calphad method.

mised. Usually a lot of time is spent in getting the start values right, in the sense that the optimising program should be able to calculate a corresponding value for each experimental datum used. Implicit data, such as the phase diagram data, are difficult to handle because their calculations involve solving nonlinear equations. If bad start values are used for the optimising variables, the nonlinear equations may not yield any solution. On the other hand the thermochemical data, for instance the enthalpy of mixing of the liquid, pose no such difficulty, since they can be explicitly calculated from the Gibbs energy model. Therefore, it is more practical to begin the optimisation with a 'minimal' data set, comprising only a few vital experimental data. Including too many experimental data in the beginning stage of the optimisation may prove unwieldy. In the case of binary systems, for example, it is enough to use data pretaining to three-phase equilibria and congruent transformations. Thermochemical information, such as enthalpy data and activity data, etc. may also be included in the minimal data set. One may also use estimated (by extrapolation) or experimental metastable equilibrium data (Fig. 2), since it reduces the number of

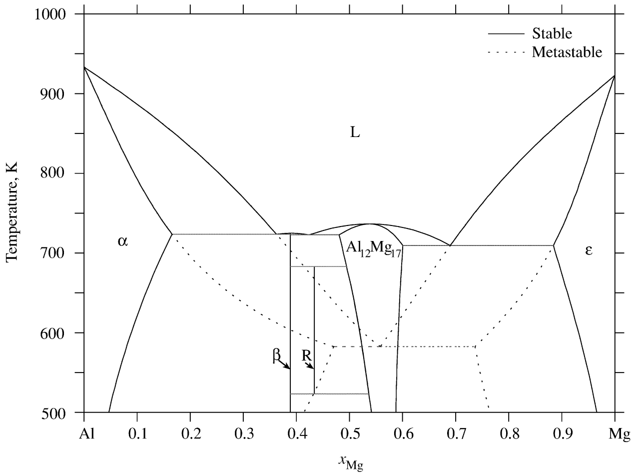

Fig. 2. Al–Mg phase diagram: stable and metastable phase boundaries.

phases that are optimised together. However, one should exclude all such estimated phase diagram data in the final stage of the optimisation.

Once a workable thermodynamic description is obtained using the minimal data set, more experimental data can be added. However, it is not recommended to use all the critically evaluated experimental data in the optimisation, since this may prove difficult to handle. In fact, one always works with an 'essential' data set. Each experimental datum in the essential data set must be weighted carefully according to its relative merits. Selection and weighting of the data are very subjective. Dependability of the experimental method and agreement between independent measurements of the same quantity should be taken into account while selecting and weighting the data. Usually constitutional data deserve more weight than thermochemical data, particularly if the thermochemical data are not established by several independent measurements.

For each experimental datum (dependent quantity) used as input, there should be a corresponding equilibrium condition specified in terms of appropriate state variables (independent quantities). This should reflect the actual experimental conditions as close as possible. Details such as temperature, pressure, phases present, compositions, etc. are usually known so that the equilibrium conditions can be easily specified. The optimising program calculates the dependent quantities at the specified equilibrium condition using the current set of optimising variables. The optimising variables are continuously adjusted until the weighted sum of squares of error is minimum.

The choice of dependent and independent quantities while defining an experiment is critical for the progress of optimisation. It is illustrated in Fig. 3 for the case of binary phase boundary data [6]. The phase boundaries in a binary system can be measured either at a fixed composition or at a fixed temperature. In the former case, composition is the independent quantity and temperature is measured: e.g. measurement of liquidus temperature by DTA of a sample at fixed composition. Therefore, the equilibrium specification normally includes a condition on the composition. In the latter case, phase composition is measured at a fixed temperature: e.g. microprobe determination of composition of a single grain annealed at a fixed temperature. Here, equilibrium specification includes a condition on the temperature. The measurement at a fixed composition is most suitable for flat phase boundaries. In this case, if one uses temperature as an equilibrium condition, it may give rise to a calculated composition that is far off from the

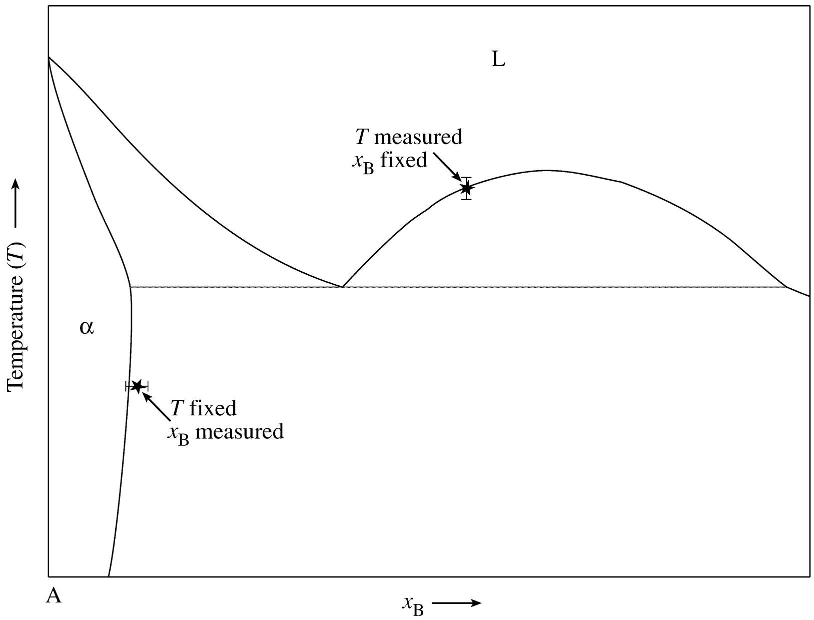

Fig. 3. Phase diagram showing regions where only composition can be reliably measured at a given temperature and vice versa.

actual value. This is because a small fluctuation in the temperature can result in a big change in the calculated composition, thus causing the sum of squares of error to increase dramatically. Conversely, the measurement at a fixed temperature is best suited for vertical phase boundaries. In this instance, setting composition as an equilibrium condition can cause abnormal increase in sum of squares of error.

Each measured quantity must have an accuracy (standard deviation) associated with it, which may be reported or estimated. Independent variables may also have a specified accuracy. For example, temperature in an annealing treatment may be controlled within an accuracy of ±5 K. Both these accuracies are significant for the optimisation, since they are used in the calculation of sum of squares of error.

If required, data should be corrected for systematic errors. Using too many data of one kind can make the optimisation biased. In order to avoid this weights on such kind of data may be reduced.

When optimising systems with insufficient experimental information, one may utilise theoretically obtained values. For example, the enthalpy of formation of transition metal compounds, estimated using Miedema's method [7], is often used in place of missing data. Similarly, the molar heat capacity of a compound may be approximated using Kopp–Neumann rule as the weighted sum of the molar heat capacities of its constituent elements. There are several thermochemical data estimation methods [8] that are based on trends and regularities, which can be quite handy. One can also infer great deal of information by comparison with similar systems. For example, there are many R–M (R = rare earth metal, M = a given element) systems which show striking regularities with respect to their thermochemistry and phase diagrams [9], so that data of one system can shed light on another system.

Information available in higher-order systems may sometimes be used in improving data in lower-order systems. For example, in Ti–X systems there is generally an experimental difficulty due to oxygen contamination of alloys. Therefore, constitutional data in the Ti-rich alloys are often unreliable. It may be possible, however, to make a good estimate of phase boundaries in Ti–X systems by extrapolating phase boundaries from Ti–X–O systems.

The generation of Gibbs energy functions from constitutional data can be thought of as the reverse of the calculation of a phase diagram using Gibbs energy functions. This might give us the impression that it is sufficient to use constitutional data alone for generating Gibbs energy functions. Estimation of Gibbs energy functions from phase diagram data is an ill-conditioned problem, and therefore very sensitive to the accuracy of the constitutional data used. Experimental data are seldom accurate enough to meet this criterion. Small changes in the constitutional data can make large fluctuations in the model parameters. Therefore, constitutional data should almost always be supplemented with thermochemical data. On the other hand, small changes in model parameters usually do not alter calculated phase boundaries in any noticeable way.

It is generally preferred to have only quantities that are actually measured as input for the optimisation. Values derived from measured quantities may not satisfy the statistical requirements for the least-squares optimisation. An optimisation software should be flexible enough to accept the experimental quantity as input, rather than a derived quantity. For example, to determine the activity of Zn (a_{Zn}) in the Ag–Zn system, one can measure the EMF (E) of the following galvanic cell:

$$\mathrm{Zn}|\mathrm{ZnCl_2} + (\mathrm{KCl} + \mathrm{LiCl})_{\mathrm{Eutectic}}|(\mathrm{Ag–Zn})$$

The EMF of this cell is related to a_{Zn} by the relation

$$\mu_{\mathrm{Zn}} - {}^{\circ}\mu_{\mathrm{Zn}} = RT \ln a_{\mathrm{Zn}} = -zFE = -2FE \tag{1}$$

where z is the number of moles of electrons involved in the cell reaction and F is the Faraday constant. Generally one tends to use a_{Zn} rather than E, because the former is the thermodynamic quantity that is usually reported and it is directly calculated by the optimising software. However, the quantity that is most suitable to be used in the optimisation is E, which is actually measured in the experiment. By rearranging Eq. (1), E can be expressed as a function of a_{Zn}:

$$E = -\frac{RT \ln a_{\mathrm{Zn}}}{2F} \tag{2}$$

Note that the activity of Ag (a_{Ag}) may not be used in the optimisation since it is calculated from a_{Zn} by Gibbs–Duhem integration.

It may not be always possible to use the measured quantities directly in the optimisation. This may be because of a software limitation or due to a mathematical difficulty. For example, in the Knudsen cell–mass spectrometric determination of activity coefficients (γ_i) of components of a binary system A–B, one measures the ion intensity (I_i) ratio as a function of composition at a given temperature. The activity coefficients of both components are simultaneously obtained by the integration of the ion intensity ratios, using the scheme proposed by Neckel and Wagner [10]:

$$^{\mathrm{xs}}G = RT\left[\int_0^{x_{\mathrm{B}}} \ln\left(\frac{I_{\mathrm{B}}x_{\mathrm{A}}}{I_{\mathrm{A}}x_{\mathrm{B}}}\right)dx_{\mathrm{B}} - x_{\mathrm{B}}C(T)\right] \tag{3a}$$

$$\left(\frac{\partial\, ^{\mathrm{xs}}G}{\partial x_{\mathrm{B}}}\right) = RT\left[\ln\left(\frac{I_{\mathrm{B}}x_{\mathrm{A}}}{I_{\mathrm{A}}x_{\mathrm{B}}}\right) - C(T)\right] \tag{3b}$$

where,

$$C(T) = \int_0^1 \ln\left(\frac{I_{\mathrm{B}}x_{\mathrm{A}}}{I_{\mathrm{A}}x_{\mathrm{B}}}\right)dx_{\mathrm{B}} \tag{3c}$$

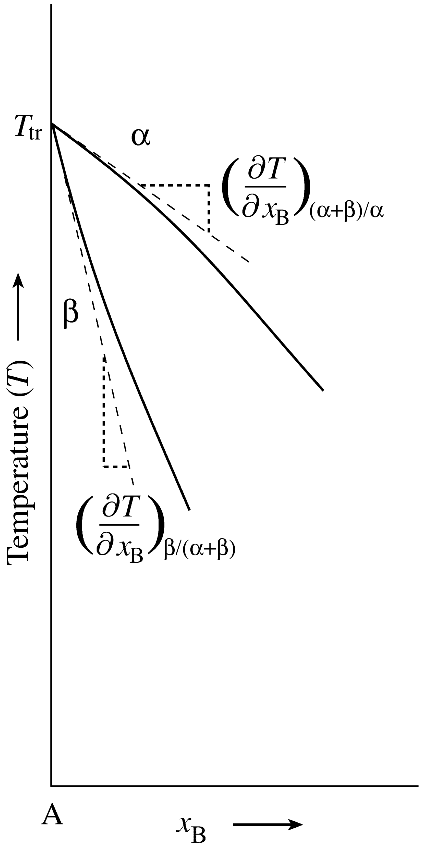

Fig. 4. Initial slopes of phase boundaries in a binary system.

The excess partial molar Gibbs energies (or activity coefficients) can be readily calculated as

$$^{xs}G_A = RT \ln \gamma_A = {}^{xs}G - x_B\left(\frac{\partial\, ^{xs}G}{\partial x_B}\right) \tag{4a}$$

$$^{xs}G_B = RT \ln \gamma_B = {}^{xs}G + (1 - x_B)\left(\frac{\partial\, ^{xs}G}{\partial x_B}\right) \tag{4b}$$

In order to use the ion intensity ratio in an optimisation, one must express it as a function of γ_i. This involves the inversion of Eqs. (4a) and (4b), which contain integrals. It is, therefore, more practical to use $^{xs}G_i$ rather than the ion intensity ratio. Note that $^{xs}G_i$ is a better choice as an input compared to γ_i, because the magnitude of the former is greater than the latter, hence easier to control in an optimisation.

Sometimes it is possible to isolate erroneous phase diagram data using simple thermodynamic reasonings [11]. For example, experimental slopes of phase boundaries involving terminal phases in a binary system may be checked for their agreement with the well-known van't Hoff equation [12]. The van't Hoff equation for initial slopes of phase boundaries is written as

$$\left(\frac{\partial T}{\partial x_B}\right)^{-1}_{\beta/(\alpha+\beta)} - \left(\frac{\partial T}{\partial x_B}\right)^{-1}_{(\alpha+\beta)/\alpha} = \frac{\Delta H_A^{\beta\rightarrow\alpha}}{RT_{tr}^2} \tag{5}$$

where $\Delta H_A^{\beta\rightarrow\alpha}$ is the enthalpy of the $\beta \rightarrow \alpha$ phase transition of A and T_{tr} is the corresponding temperature. This is illustrated in Fig. 4. If the phase boundaries violate the van't Hoff equation, it will not be possible to reproduce them in a thermodynamic optimisation.

In some instances of optimisation it may be necessary to consider experimental data from several higher-order systems. This is particularly true in the case of terminal phases that exist only in a narrow region in a binary system. Although such phases can be described satisfactorily by more than one set of model parameters in the binary, not all sets are suitable in a higher-order system. An example is the austenite phase (γ) in the Fe–Ti system (Fig. 5), which exists as the γ-loop near the Fe-rich corner. It dissolves very small amounts of C and N, for which very accurate experimental data exist. This low solubility can not be easily modelled by introducing ternary terms.

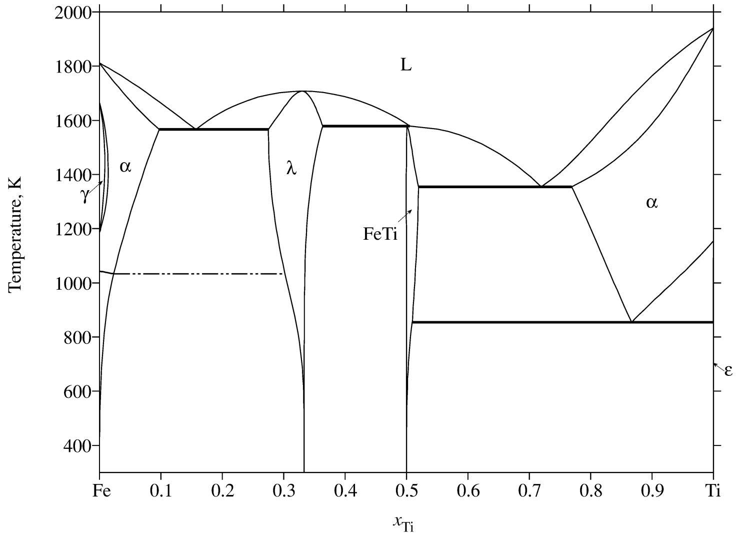

Fig. 5. Fe–Ti phase diagram.

However, it is very sensitive to the binary γ phase description. Therefore, it is best to optimise the description of the binary γ, treating data from Fe–Ti, C–Fe–Ti, and Fe–N–Ti together. Otherwise one may need to use very large ternary interaction terms for the γ phase.

3. Gibbs energy models

Choice of the Gibbs energy model for a phase should be such that it is physically sound and adequate for the $P-T-x$ domain in which the phase is stable. The model should have reasonable extrapolation characteristics in the higher-order systems. Compatibility with existing models is crucial, if the resulting thermodynamic description is to be added to an existing database or it has to be combined with another description.

In general physically sound models are more informative and need less adjustable parameters to fit the experimental data. However, as physical soundness of the model increases computational difficulty increases. From Calphad point of view it is a good strategy to start the optimisation using simple Gibbs energy models which have only few model parameters. Parameters of simple models can easily be identified with the physicochemical characteristics of the phase, thus providing good insight into the physics and chemistry of the phase formation. For example, as a first approximation one may treat all intermediate phases in a binary system as stoichiometric compounds. Once a satisfactory thermodynamic description is obtained, models may be changed to more appropriate ones. The parameter values obtained using simple models can often be used as starting values for parameters of more elaborate models.

The sublattice model [13,14] is one of the most commonly used Gibbs energy models. In the present form [15] it is capable of treating many types of phases having arbitrary numbers of constituents and sublattices. When applied to intermediate phases, it is usually referred as the Compound Energy Formalism (CEF) [16]. The CEF is one of the most important approaches to treat phases using the sublattice model. The flexibility of the sublattice model makes it very suitable for computer calculations, whereas the same flexibility introduces some problems. It may be possible that a solid-phase can be modelled satisfactorily using more than one sublattice formulation. This leads to model incompatibilities, especially when one wants to combine thermodynamic descriptions of systems where different sublattice models are used for the same phase. For example, models used for the μ phase in Co–Nb and Nb–Ni should be the same, if they have to be combined in the description of the Co–Nb–Ni system. Therefore, one must be careful in defining the sublattice formulation for a phase, since the model should also be adequate to treat the same kind of phase in other systems. For solid-phases, an approach based on crystal structure and homogeneity range is recommended [17,18]. The sublattice model should follow crystallographic sublattices, although simplifications are often necessary to avoid too many end-members. When selecting a sublattice model for a phase, due credit must be given to known crystallographic and solubility range data for the phase, not only in the system under consideration, but also in other systems (binary as well as higher-order) where the same phase is observed [19]. Sometimes it is also necessary to consider information regarding other phases with related structures, as in the case of phases related by order-disorder phase transitions (e.g. the A2↔B2 transition in the Cu–Zn system). Crystallographic information is mainly used for deciding the number of sublattices to be used and for assigning constituent species to each of them. An intermediate phase usually has a preferred stoichiometry, called the 'ideal' stoichiometry, where each sublattice is occupied by only one constituent species. But in reality some sublattices may have mixing of species. The mixing characteristics, in general, should commensurate with the data on the homogeneity range and/or crystallographic information of the phase. By this approach one can ensure the general applicability of the model.

The main difficulty with the sublattice model is that the number of end-members becomes too large (also the number of model parameters) as the number of sublattices and constituents increases. It is often a problem to find suitable energy parameters for many of the fictitious end-members, since they cannot be estimated in a meaningful manner in an optimisation. Then one should look into the possibility of reducing the number of such energy parameters. The number of sublattices may be reduced by grouping together sublattices with same point group symmetry and/or coordination number. In many cases reducing the number of parameters amounts to somehow relating them. In other instances it may be possible to fix the values of some parameters. For example, in the case of tetrahedral close-packed phases one can approximate the Gibbs energy of an end-member to be equal to the weighted sum of the Gibbs energies of the constituents in their fcc and bcc state. The fcc state is used for constituents with coordination number 12, while the bcc state is used for higher coordination numbers [17].

If phases with the same crystal structure appear in more than one region in the phase diagram, they should be treated as one phase in the modelling, so that it has only one Gibbs energy description that is valid in all regions. For example, the bcc phase appearing near the Fe-side and Ti-side of the Fe–Ti system (Fig. 5) should be represented by a single Gibbs energy description.

The thermodynamic description of a subsystem, which is part of different higher-order systems, must be the same, if the higher-order systems are to be combined. For example, the thermodynamic description of a quaternary system is based on four ternary systems. Each of the ternary system requires description of three binary systems. Since each binary system is common to two ternary systems, the description of a given binary should be the same in both the ternaries, failing which the ternaries can not be combined. Similarly, it is quite necessary to stick to one common set of Gibbs energy descriptions for unaries, when different binaries, ternaries, etc. have to be combined to form a large database.

An intermediate phase having a narrow homogeneity range may be modelled as a Wagner–Schottky phase [20,21]. It is illustrated for the case of the Laves phase (λ) in the Fe–Ti system. This Laves phase has a $C14$ structure and its ideal stoichiometry corresponds to Fe_2Ti. A two-sublattice model, $(Fe\%,Ti)_2$:$(Fe,Ti\%)_1$, is generally used for describing this phase ('%' denotes the major constituent of the sublattice). The Gibbs energy for one mole of formula unit of the Laves phase is given by

$$\begin{aligned} G^{\lambda} = {}& {}^1y_{\mathrm{Fe}}({}^2y_{\mathrm{Ti}}{}^{\circ}G^{\lambda}_{\mathrm{Fe:Ti}} + {}^2y_{\mathrm{Fe}}{}^{\circ}G^{\lambda}_{\mathrm{Fe:Fe}}) \\ & + {}^1y_{\mathrm{Ti}}({}^2y_{\mathrm{Ti}}{}^{\circ}G^{\lambda}_{\mathrm{Ti:Ti}} + {}^2y_{\mathrm{Fe}}{}^{\circ}G^{\lambda}_{\mathrm{Ti:Fe}}) \\ & + RT[2({}^1y_{\mathrm{Fe}}\ln{}^1y_{\mathrm{Fe}} + {}^1y_{\mathrm{Ti}}\ln{}^1y_{\mathrm{Ti}}) \\ & + 1({}^2y_{\mathrm{Fe}}\ln{}^2y_{\mathrm{Fe}} + {}^2y_{\mathrm{Ti}}\ln{}^2y_{\mathrm{Ti}})] \\ & + {}^1y_{\mathrm{Fe}}{}^1y_{\mathrm{Ti}}({}^2y_{\mathrm{Fe}}L^{\lambda}_{\mathrm{Fe,Ti:Fe}} + {}^2y_{\mathrm{Ti}}L^{\lambda}_{\mathrm{Fe,Ti:Ti}}) \\ & + {}^2y_{\mathrm{Fe}}{}^2y_{\mathrm{Ti}}({}^1y_{\mathrm{Fe}}L^{\lambda}_{\mathrm{Fe:Fe,Ti}} + {}^1y_{\mathrm{Ti}}L^{\lambda}_{\mathrm{Ti:Fe,Ti}}) \\ & + {}^1y_{\mathrm{Fe}}{}^1y_{\mathrm{Ti}}{}^2y_{\mathrm{Fe}}{}^2y_{\mathrm{Ti}}L^{\lambda}_{\mathrm{Fe,Ti:Fe,Ti}} \end{aligned} \quad (6)$$

where ${}^sy_i$ is the site fraction of the constituent species i on sublattice s, $G^{\lambda}_{I(0)}$ is the Gibbs energy per mole of formula unit of the end member compound $I(0)$, and $L^{\lambda}_{I(z)}$ is the interaction energy term representing the interaction between constituent species within each sublattice of the constituent array $I(z)$. Since Ti and Fe are present only in small amounts (as defects) in the first and second sublattices, respectively, the Laves phase may be considered as a Wagner–Schottky phase. In such a case the following relation among the G parameters of Eq. (6) exists:

$$^{\circ}G^{\lambda}_{\mathrm{Ti:Fe}} = {}^{\circ}G^{\lambda}_{\mathrm{Fe:Fe}} + {}^{\circ}G^{\lambda}_{\mathrm{Ti:Ti}} - {}^{\circ}G^{\lambda}_{\mathrm{Fe:Ti}} \quad (7)$$

Note that this approach eliminates the need to optimise the parameter ${}^{\circ}G^{\lambda}_{\mathrm{Ti:Fe}}$, which is otherwise not possible to obtain in a meaningful manner. Phases having relatively large homogeneity range, such as the σ phase in Fe–V system, must not be treated as Wagner–Schottky phase.

4. Constraints on model parameters

In certain instances some model parameters are interdependent because of the physicochemical character of the phase, so that there may be one or more constraining relations among them. This effectively reduces the number of independent model parameters. One such constraint (Eq. (7)) was already given in the previous section. Here we shall discuss some more cases.

In several metallic liquids it is observed that there is definite relation between the enthalpy of mixing (ΔH) and the excess entropy (${}^{\mathrm{xs}}S$). This lead many investigators to formulate quantitative relation between ΔH and ${}^{\mathrm{xs}}S$. One such recent formulation is Tanaka's model [22] for predicting (${}^{\mathrm{xs}}S$) from a knowledge of ΔH of binary liquid alloys. This is particularly useful when dealing with a liquid phase for which there is a wealth of experimental information on ΔH, but no information on the component activities. For the simple case of a binary random solution phase, the expression for molar Gibbs energy may be written as

$$\begin{aligned} G_{\mathrm{m}} = {}& \sum_{i=\mathrm{A,B}} x_i{}^{\circ}G_i + RT\sum_{i=\mathrm{A,B}} x_i \ln x_i \\ & + x_{\mathrm{A}}x_{\mathrm{B}}\sum_{\nu=0}^{n} {}^{\nu}L_{\mathrm{A,B}}(x_{\mathrm{A}} - x_{\mathrm{B}})^{\nu} \end{aligned} \quad (8)$$

The temperature dependence of the Redlich–Kister coefficients ${}^{\nu}L_{\mathrm{A,B}}$ usually has the form:

$${}^{\nu}L_{\mathrm{A,B}} = a_{\nu} + b_{\nu}T$$

It can be shown that for a liquid phase whose molar Gibbs energy is given by Eq. (8),

$$\left.\frac{\Delta H}{{}^{\mathrm{xs}}S}\right|_{x_{\mathrm{B}}\to 0} = \left.\frac{H_{\mathrm{B}}}{{}^{\mathrm{xs}}S_{\mathrm{B}}}\right|_{x_{\mathrm{B}}\to 0} = -\frac{\sum_{\nu=0}^{n} a_i}{\sum_{\nu=0}^{n} b_i} = k \quad (9)$$

The value of k is given by Tanaka's model. Sometimes it is possible to extend this kind of constraint to the solid-phases [23]. For an intermediate phase with no information on its Gibbs energy of formation, one may assume that at its stable or metastable congruent melting point, the ratio of its enthalpy and entropy of formation has the same value as the ratio of the enthalpy of mixing and excess entropy of mixing of the liquid phase at the same temperature [24].

Sometimes, the nature of the phase diagram itself necessitates the use of constraining relations of model parameters. For example, phases exhibiting miscibility gaps are difficult to handle in an optimisation. In order to have better control of the description of the miscibility gap, constraints may be introduced on the model parameters. For example, in a binary system A–B, the constraint

$$f(T) = \left.\left(\frac{\partial^2 G_{\mathrm{m}}}{\partial x_{\mathrm{B}}^2}\right)\right|_{x_{\mathrm{B}}=x_{\mathrm{B}}^{\mathrm{Cr.}}} = \left.\left(\frac{\partial^3 G_{\mathrm{m}}}{\partial x_{\mathrm{B}}^3}\right)\right|_{x_{\mathrm{B}}=x_{\mathrm{B}}^{\mathrm{Cr.}}} = 0 \quad (10)$$

guarantees a specific critical temperature ($T_{\mathrm{Cr.}}$) for a given critical composition ($x_{\mathrm{B}}^{\mathrm{Cr.}}$) of the miscibility gap. At the critical point, where $T = T_{\mathrm{Cr.}}$ and $x_{\mathrm{B}} = x_{\mathrm{B}}^{\mathrm{Cr.}} = \frac{1}{2}$ (symmetric with respect to composition, which is of the most common occurrence), and noting that $x_{\mathrm{A}} + x_{\mathrm{B}} = 1$, we can transform Eq. (10) into an appropriate constraint:

$$2RT_{\mathrm{Cr.}} - {}^{0}L_{\mathrm{A,B}} + {}^{2}L_{\mathrm{A,B}} = {}^{1}L_{\mathrm{A,B}} - {}^{3}L_{\mathrm{A,B}}$$

so that

$$T_{\mathrm{Cr.}}=\frac{a_0+6(a_1-a_3)-a_2}{2R-(b_0+6(b_1-b_3)-b_2)} \tag{11}$$

Note that the critical point of a symmetric miscibility gap does not depend on ${}^{\nu}L_{\mathrm{A,B}}$ parameters for which $\nu>3$. For an asymmetric miscibility gap, one can again utilise Eq. (11) to derive constraints among the model parameters. For example, when $\nu=2$, we have [25],

$$\begin{aligned}{}^{0}L_{\mathrm{A,B}}=&\frac{6x_{\mathrm{B}}^{\mathrm{Cr.}}(1-x_{\mathrm{B}}^{\mathrm{Cr.}})-1}{4[x_{\mathrm{B}}^{\mathrm{Cr.}}(1-x_{\mathrm{B}}^{\mathrm{Cr.}})]^2}RT_{\mathrm{Cr.}}\\&-{}^{2}L_{\mathrm{A,B}}[24x_{\mathrm{B}}^{\mathrm{Cr.}}(1-x_{\mathrm{B}}^{\mathrm{Cr.}})-7]\end{aligned} \tag{12a}$$

$${}^{1}L_{\mathrm{A,B}}=(1-2x_{\mathrm{B}}^{\mathrm{Cr.}})\left[\frac{RT_{\mathrm{Cr.}}}{12[x_{\mathrm{B}}^{\mathrm{Cr.}}(1-x_{\mathrm{B}}^{\mathrm{Cr.}})]^2}-4\,{}^{2}L_{\mathrm{A,B}}\right] \tag{12b}$$

In the sublattice modelling of intermediate phases with homogeneity range, it may be possible that two ‘end members’ have very close compositions. It is then quite reasonable to assume that their Gibbs energies are approximately the same [26]. An example is provided by the μ phase, for which the sublattice model is

$(\mathrm{A\%,B})_1$:$(\mathrm{B})_4$:$(\mathrm{A,B\%})_2$:$(\mathrm{A})_6$

The end members of this model are: A_9B_4, A_8B_5, A_7B_6, and A_6B_7. Since most of the μ phases occur around either A_7B_6 or A_6B_7 stoichiometry, the ideal stoichiometry could be either of these. Since these two stoichiometries are very close to each other, it is advantageous to constrain their Gibbs energies to be approximately the same. The same argument may be extended in approximating Gibbs energies of two compounds with nearly the same stoichiometries.

Generally speaking entropy and enthalpy should have the same sign, unless there is a special reason for the contrary. For example, in the case of a stoichiometric compound A_pB_q whose Gibbs energy function is given by

$$\frac{{}^{\circ}G^{\mathrm{A}_p\mathrm{B}_q}-p{}^{\circ}G_{\mathrm{A}}-q{}^{\circ}G_{\mathrm{B}}}{(p+q)}=a+bT \tag{13}$$

where the coefficients a and b usually have opposite signs. Any deviation from this requires a close scrutiny.

When dealing with narrow two-phase regions of solution phases, the concept of allotropic phase boundary (T_0-line) is useful in approximating the Gibbs energy of one of the two phases from a knowledge of the Gibbs energy of the other. Along the allotropic phase boundary, which lie in the two-phase region, the Gibbs energies of both the phases are equal, i.e.

$$G_{\mathrm{m}}^{\alpha}(P,T,x_i)-G_{\mathrm{m}}^{\gamma}(P,T,x_i)\big|_{P=P_0,T=T_0,x_i=x^0_{i=1\,\mathrm{to}\,(c-1)}}=0 \tag{14a}$$

For the binary system A–B the allotropic phase boundary is defined by,

$$G_{\mathrm{m}}^{\alpha}(P_0,T_0,x_{\mathrm{B}}^0)-G_{\mathrm{m}}^{\gamma}(P_0,T_0,x_{\mathrm{B}}^0)=0 \tag{14b}$$

At a pressure P_0 and a temperature T_0, Eq. (14b) may be solved to obtain the composition x_{B}^0. When the two-phase region is narrow, it is reasonable to assume that the allotropic phase boundary bisects the tie-lines in an isobaric $T-x$ phase diagram. Therefore, at T_0 the composition x_{B}^0 is given by

$$x_{\mathrm{B}}^0=\frac{x_{\mathrm{B}}^{\alpha}+x_{\mathrm{B}}^{\gamma}}{2}$$

Hence, by knowing the Gibbs energy function of one of the phases and few tie-lines at different temperatures, we can estimate the Gibbs energy of the other phase as a function of temperature and composition. The estimated Gibbs energy values may be used as input for the optimisation, especially when there are no experimental thermochemical data available. An example where this approach could be useful is in the optimisation of the γ-loop (Fig. 6) in many Fe binaries (e.g. Fe–Ti, Fe–V, Fe–W, etc.), where there is a wealth of thermochemical data available for the α phase and not enough data for the γ phase.

In some cases the model requires that, due to the crystallographic symmetry of the phase, several model parameters be related. This is illustrated in the modelling of B2 phase (CsCl structure). In the sublattice formalism, one mole of B2 phase in the binary system A–B is denoted by

$(\mathrm{A\%,B})_{1/2}$:$(\mathrm{A,B\%})_{1/2}$

The molar Gibbs energy of the phase is given by

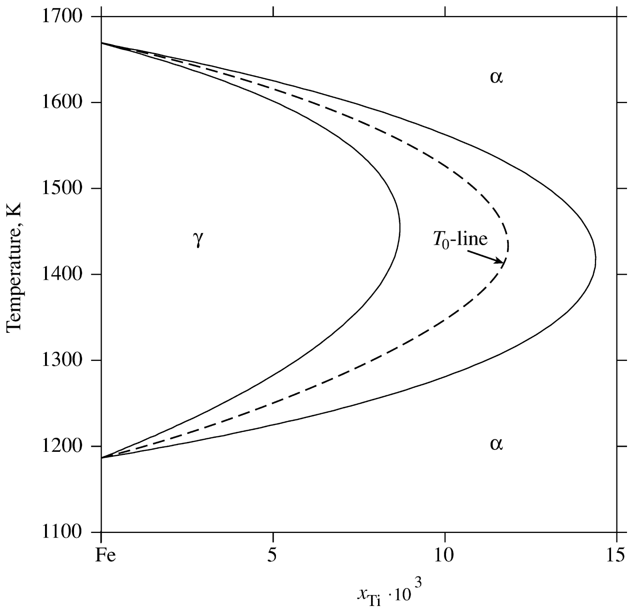

Fig. 6. γ-loop in the Fe–Ti system and the corresponding T_0-line.

$$
\begin{aligned}
G^{\mathrm{B2}} = {}& {}^{1}y_{\mathrm{A}}({}^{2}y_{\mathrm{B}}{}^{\circ}G^{\mathrm{B2}}_{\mathrm{A:B}} + {}^{2}y_{\mathrm{A}}{}^{\circ}G^{\mathrm{B2}}_{\mathrm{A:A}}) \\
& + {}^{1}y_{\mathrm{B}}({}^{2}y_{\mathrm{B}}{}^{\circ}G^{\mathrm{B2}}_{\mathrm{B:B}} + {}^{2}y_{\mathrm{A}}{}^{\circ}G^{\mathrm{B2}}_{\mathrm{B:A}}) \\
& + RT\left[\frac{1}{2}({}^{1}y_{\mathrm{A}}\ln{}^{1}y_{\mathrm{A}} + {}^{1}y_{\mathrm{B}}\ln{}^{1}y_{\mathrm{B}})\right. \\
& \left. + \frac{1}{2}({}^{2}y_{\mathrm{A}}\ln{}^{2}y_{\mathrm{A}} + {}^{2}y_{\mathrm{B}}\ln{}^{2}y_{\mathrm{B}})\right] \\
& + {}^{1}y_{\mathrm{A}}{}^{1}y_{\mathrm{B}}\left({}^{2}y_{\mathrm{A}}\sum_{\nu=0}^{n}{}^{\nu}L^{\mathrm{B2}}_{\mathrm{A,B:A}}({}^{1}y_{\mathrm{A}} - {}^{1}y_{\mathrm{B}})^{\nu}\right. \\
& \left. + {}^{2}y_{\mathrm{B}}\sum_{\nu=0}^{n}{}^{\nu}L^{\mathrm{B2}}_{\mathrm{A,B:B}}({}^{1}y_{\mathrm{A}} - {}^{1}y_{\mathrm{B}})\right)^{\nu} \\
& + {}^{2}y_{\mathrm{A}}{}^{2}y_{\mathrm{B}}\left({}^{1}y_{\mathrm{A}}\sum_{\nu=0}^{n}{}^{\nu}L^{\mathrm{B2}}_{\mathrm{A:A,B}}({}^{2}y_{\mathrm{A}} - {}^{2}y_{\mathrm{B}})^{\nu}\right. \\
& \left. + {}^{1}y_{\mathrm{B}}\sum_{\nu=0}^{n}{}^{\nu}L^{\mathrm{B2}}_{\mathrm{B:A,B}}({}^{2}y_{\mathrm{A}} - {}^{2}y_{\mathrm{B}})\right)^{\nu} \\
& + {}^{1}y_{\mathrm{A}}{}^{1}y_{\mathrm{B}}{}^{2}y_{\mathrm{A}}{}^{2}y_{\mathrm{B}}L^{\mathrm{B2}}_{\mathrm{A,B:A,B}} \qquad (15)
\end{aligned}
$$

Since sublattices ‘1’ and ‘2’ are indistinguishable because of the crystallographic symmetry, the following constraints on the model parameters must be met.

$$ {}^{\circ}G^{\mathrm{B2}}_{\mathrm{A:B}} = {}^{\circ}G^{\mathrm{B2}}_{\mathrm{B:A}} $$

$$ {}^{\nu}L^{\mathrm{B2}}_{\mathrm{A,B:A}} = {}^{\nu}L^{\mathrm{B2}}_{\mathrm{A:A,B}} $$

$$ {}^{\nu}L^{\mathrm{B2}}_{\mathrm{A,B:B}} = {}^{\nu}L^{\mathrm{B2}}_{\mathrm{B:A,B}} $$

5. Performing the optimisation

Success of an optimisation depends on:

1. the selected models
2. the selected experimental data
3. the number of model parameters
4. what parameters can be meaningfully optimised using the selected experimental data
5. starting values for model parameters, and
6. the order in which parameters are optimised.

The optimisation software like PARROT (a module of the *Thermo-Calc* data bank system) and the Lukas program have the facility to generate start values for the model parameters. If such built-in procedure fails, then one should resort to heuristic methods. Sometimes it may be possible to use model parameters obtained for a similar system as start values for the optimisation.

Thermodynamic optimisation is a stepwise procedure. It is a good strategy to exclude all intermediate phases during the initial stages of the optimisation. In other words, one starts the optimisation with just the liquid and the terminal phases. Since intermediate phases are not present during this stage of the optimisation, one may have to use extrapolated metastable equilibrium data (Fig. 2). When a feasible description of the liquid and the terminal phases is obtained, the description of the intermediate phases may be optimised by keeping the optimising variables for other phases fixed. One could speed up the procedure by excluding irrelevant experimental data from the optimisation. This may be done by setting the weights on such data to zero. For example, while optimising the parameters for fcc phase, one may exclude the data concerning the equilibrium involving bcc, hcp, and liquid. In this respect it is handy to have labels or numbers for each experimental datum in the essential data set and a table with names of phases against the data numbers or labels where the phase is present. Of course, in the final run of the optimisation all the data are considered together with all the parameters that are being optimised.

One of the objectives in the optimisation should be to obtain a description with fewer number of model parameters, yet with a lower sum of squares of error. For example, in modelling simple binary metallic solution phases one rarely needs a Redlich–Kister polynomial [27] of degree more than two. Exceptions are phases exhibiting an enthalpy of mixing that has an extremum displaced from the equiatomic composition or a miscibility gap close to the edge of the phase diagram. To model such phases one usually needs higher-order polynomials. It is not recommended to simply increase the number of model parameters, in order to get a description that represents all the data as close as possible.

With more model parameters the sum of squares of error usually decreases, but at the same time the parameters may become large in magnitude and opposing in sign. This usually has a adverse effect on the extrapolation characteristics of the model. Such parameters may either be excluded from the description or given a fixed value. A well determined parameter is unlikely to have extremely large or small magnitude, when expressed for one mole of atoms.

It is meaningless to optimise certain parameters when there is no suitable thermochemical data that contribute to its significance. The relative standard deviation of a parameter can be taken as a measure of its significance. A large relative standard deviation means the parameter is badly determined and therefore should not be included in the optimisation. For example, including a $T \ln T$ parameter in the description of ${}^{\mathrm{xs}}G$ of a solution phase makes no sense, unless there is enough data to support the T dependence of ΔH or ${}^{\mathrm{xs}}S$. Thus it is important to check the magnitudes and standard deviations of the optimising variables frequently during the optimisation. In some instances constraints such as Eq. (7) on badly determined parameters may be used.

It is quite unnecessary to report too many significant digits for the model parameters, since the effect of trailing digits on Gibbs energy is generally insignificant [28]. The model parameters may be rounded off during the optimisation. One usually starts with rounding off the parameter with the highest relative standard deviation. The optimisation is rerun while keeping the value of the rounded off parameter fixed. The rounding off should be done in such a way that there is no significant increase in the sum of squares of error. The procedure is continued until all parameters except one are rounded off.

During the course of the optimisation one may find that that certain experimental data are difficult to fit. Such data are most likely to be erroneous and should be subjected to close scrutiny.

Calculating the phase diagram at different stages of the optimisation and comparing it with the experimental data is often useful. This may reveal several nonconformities, like metastable regions becoming stable, which may demand a change in the optimisation strategy. Ensuring correct phase stability is very important, since the thermodynamic description should be free of errors such as phases which decompose or become stable where they should not. In this regard, $T-\mu_i$ diagrams can be quite handy. After the final run of the optimisation, it may be necessary to perform some calculations outside the range of experimental data, in order to make sure that the description has acceptable extrapolation features. For example, one may calculate the phase diagram of a binary system starting from a temperature well above the melting point of the highest melting component down to 298 K, even if the available experimental data do not cover the whole temperature range.

One should always check if the equilibrium calculated by the optimising software is the intended one. For instance, in the case of a congruently melting compound in a binary system it is possible that the program may calculate a tie-line involving the liquid and compound that is on the wrong side, thus causing the sum of squares of error to increase. A similar situation can occur in a miscibility gap region, where it is always a possible to find a composition that is not the desired one.

An optimisation is seldom concluded without possibility of further improvement. The Calphad method is an iterative procedure and the results from the computerised evaluation may sometimes force the assessor to alter models, change essential data sets, and/or revise weights. The decision to conclude an optimisation generally depends on a balanced combination of the following factors: an acceptable agreement between calculated and experimental data, reasonable magnitudes for the parameter values and their standard deviations, good extrapolation characteristics. Whenever new data become available, one should check their reproducibility by performing a calculation using the existing thermodynamic description.

6. Conclusions

We have presented some guidelines that may help a novice user of computer programs for optimising phase diagrams using the Calphad method. These guidelines are rather general, and one should realise that there are always specific difficulties associated with a particular system. Nevertheless, the authors feel that these hints are useful for a beginner.

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