

1 Introduction

The Calphad technique has reached maturity. It started from a vision of combining data from thermodynamics, phase diagrams, and atomistic properties such as magnetism into a unified and consistent model. It is now a powerful method in a wide field of applications where modeled Gibbs energies and derivatives thereof are used to calculate properties and simulate transformations of real multicomponent materials. Chemical potentials and the thermodynamic factor (second derivatives of the Gibbs energy) are used in diffusion simulations. The driving forces of the phases are used to simulate the evolution of microstructures on the basis of the Landau theory. In solidification simulations the fractions of solid phases and the segregation of components, as well as energies of metastable states, which are experimentally observed by carrying out rapid solidification, are used. Whenever the thermodynamic description of a system is required, the Calphad technique can be applied.

The successful use of Calphad in these applications relies on the development of multicomponent databases, which describe many different kinds of thermodynamic functions in a consistent way, all checked to be consistent with experimental data. The construction of these databases is still a very demanding task, requiring expertise and experience. There are many subjective factors involved in the decisions to be made when judging and selecting which among redundant experimental data are the most trustworthy. Even more subjective is the assessment of phases of which little or nothing is known, except perhaps in a narrow composition and temperature range. Furthermore, the growing range of applications of these databases increases the feedback and several corrections and modifications are required. The development of new models and the rapid advance of first-principles (from the Latin *ab initio*) calculations makes the assessment techniques very dynamic and challenging.

1.1 Computational thermodynamics

Thermodynamics describes the equilibrium state of a system. This is a necessary foundation for simulations of phase transitions and processes, since all systems try to reach this state. In computational thermodynamics (CT) the equilibrium state is described using thermodynamic functions that depend on temperature, pressure, and composition.

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These functions can be extrapolated also outside the equilibrium state and thus, when they are included in a simulation model, provide information about values and gradients of the thermodynamic properties in space and time outside the range of stability of a phase.

The thermodynamic models used by CT contain adjustable parameters, which can be optimized in such a way that the models can reproduce many kinds of experimental data as well as theoretical models and first-principles data. Thus CT is more flexible and has much wider possibilities for realistic application calculations than merely using first-principles data. The quality of the results of CT is based on the fit to experimental data, which is also the criterion in judging the quality of results from first-principles calculations.

More fundamental theories are focused on understanding particular mechanisms and isolated properties, which they do very well, but they are not able to describe their coupling in complex systems. CT can make use of theoretical results as well as traditional experimental data and provides a unique framework of various types of information that can be obtained using rather simple models. Thus CT is able to provide consistent thermodynamic information with the accuracy required to describe multicomponent systems of technological interest. It is versatile enough to be extended to new applications and incorporate related types of information such as magnetism (see section 5.4.2) and viscosity (Seetharaman *et al.* 2005).

The important fact is that the thermodynamic information which can be extracted from CT can describe the equilibrium state as well as extrapolations from it. There are types of simulation software used today that depend on thermodynamic information such as heat capacities, partition coefficients, and latent heats, but for which the data have been collected from various sources and are inconsistent and cannot reproduce the real equilibrium state. The results from simulations using such software may be reasonable because the kinetic model has parameters that can be adjusted to compensate for the errors in the thermodynamic data, but the range of applicability of the simulation is poor. Of course, even with correct thermodynamics one will have to fit kinetic parameters in simulation models, but these will have a larger range of validity because they depend less on the thermodynamic properties of the system.

CT has shown its importance for calculating multicomponent phase diagrams and for process and phase-transformation simulations as mentioned above and in detail described in section 8.10. It is used by experimental researchers as a tool to test the compatibility between their results and for data found in the literature, as well as planning new experimental work. CT is also interesting to theoreticians, not only to use as a “reality” against which they can check their predictions from fundamental models but, also and more importantly, as a technique to improve the usefulness of their results by combining them with experimental data, i.e. the Calphad method.

Knowledge of phase equilibria is fundamental to all aspects of materials science, since the properties are determined by the microstructure, see for example Durand-Charre (2004), and the microstructure consists of several phases arranged in space as in Fig. 1.1. A practical way to obtain the phase equilibria in a multicomponent system is by calculations using assessed thermodynamic databases. Hence the generation of reliable and consistent computer-readable thermodynamic databases is very important.

1.2 The past and present, the Calphad technique

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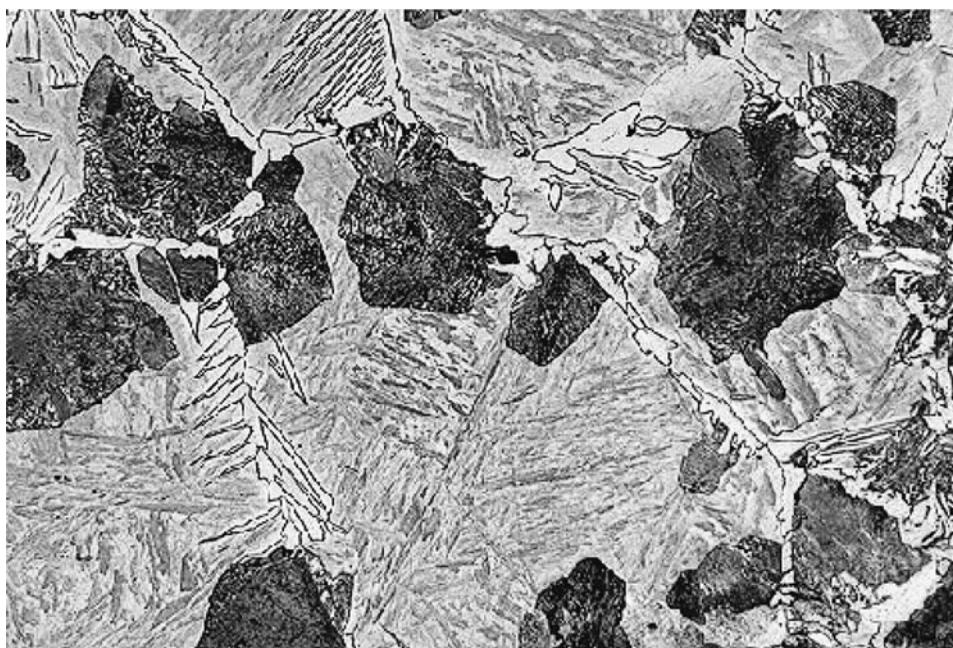


Figure 1.1 The microstructure of a low-carbon steel with many different stable and metastable phases formed during cooling. The properties of the material depend on the amounts and arrangements of these phases and their compositions. Computational thermodynamics together with application software can be used to simulate the development of such microstructures and predict the properties of materials. Courtesy of Mats Hillert.

New experiments are still very important, because the validated databases are based on the combination of theoretical and experimental data.

1.2 The past and present, the Calphad technique

Phase diagrams had been calculated from Gibbs-energy models by van Laar (1908a, 1908b) and many others, but the first general description of Calphad was written by Larry Kaufman in the book *Computer Calculations of Phase Diagrams* (Kaufman and Bernstein 1970), in which he developed the important concept of “lattice stability” which he had introduced earlier (Kaufman 1959). He explained clearly how parameters could be derived both from experimental phase diagrams and from the rudimentary first-principles techniques available at that time, and how they could be used to calculate phase diagrams. The concept of lattice stability was essential for the development of multicomponent thermodynamic databases, which was a very far-sighted goal because at that time it was a challenge to calculate even a ternary phase diagram.

The method of extrapolating solubility lines into the metastable range to obtain a thermodynamic property, such as the melting temperature of metastable fcc Cr, shows one of the important advantages of combining phase diagrams and thermodynamics.

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Many such combinations have been used in exploring properties of other systems during the development of the Calphad techniques. Important contributions on how to use experimental and theoretical data in thermodynamic models were made by Kubaschewski *et al.* (1967), Hillert and Staffanson (1970), Hasebe and Nishizawa (1972), Ansara *et al.* (1973), and Lukas *et al.* (1977). For historic details, the recent paper by Kaufman (2002) is recommended.

Originally the term “Calphad” meant calculating phase diagrams from thermodynamic models with parameters adjusted to the available experimental data. The term “Calphad technique” has come to mean the technique of selecting models for phases that can be extrapolated both in composition and in temperature ranges, including also metastable ranges. A comprehensive description of this Calphad technique can be found in Kattner (1997). The “Calphad method” means the use of all available experimental and theoretical data to assess the parameters of the Gibbs energy models selected for each phase. That is the topic of this book. To describe the use of these models and parameters stored in thermodynamic databases for various applications, the term “computational thermodynamics” has been adopted.

It may be instructive to mention here that in the early days of Calphad there was a heated argument among material scientists about how to model a dilute solution. The thermodynamic properties of a dilute solution of B in a solvent A can be modeled with a simple Henrian coefficient as described in section 5.5.9. With the Calphad technique one needed two parameters, one representing the solvent phase consisting of pure B, i.e. a “lattice stability,” and one interaction parameter between A and B. In the dilute range the sum of these two parameters is the only important quantity and is in fact identical to the Henrian coefficient. The fact that the Calphad technique needed more parameters, and that the parameter representing pure B in the same phase as A often was an unstable phase (like pure fcc Cr), was taken to be a severe drawback of the Calphad technique.

However, the drawback of dilute models is more severe because there are many cases, for example at solidification, for which one must find a way to describe how the thermodynamic properties vary when the solvent phase changes. Upon investigating this problem in more detail, one finds that the Calphad technique is the simplest and most consistent way to handle a multicomponent thermodynamic system with many “solvent” phases. Similar modeling problems in which one has to evaluate “lattice stabilities” of phases with more or less limited solubilities occur often in Calphad assessments. This is discussed in chapter 6.

1.3 The future development of databases and software applications

As computers become faster, models and techniques of greater sophistication and accuracy are being developed within CT. However, there is an important “inertia” present in the thermodynamic databases, which are compiled from a large number of both independent and inter-dependent assessments. In a reference book like Hultgren *et al.* (1973) one may replace the data for one element without changing anything else, but in a database the binary assessments depend on the unary data for pure elements and on the models selected

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for the phases. Ternary and higher-order assessments depend on the selected assessments of the corresponding lower-order systems. This means that, in order to introduce a new value for a pure element, a new assessment of a binary system, or a new model for a phase present in a thermodynamic database one must revise all assessments depending on this value, assessment, or model. The current commercial databases depend on a number of decisions taken for pure elements and models made more than 20 years ago by the Scientific Group Thermodata Europe (SGTE, <http://www.sgte.org>). It is a great credit to the scientists involved in these decisions that there have been so few problems with using these data to build multicomponent databases for so many years. Nonetheless, there is a need to revise the set of unary and binary data as well as models continuously and maybe every 10 years one should start creating improved versions of the databases from a new revised set of data. The maintaining of databases is briefly discussed in chapter 8.

The number of publications on thermodynamically assessed systems is increasing rapidly and most of them use SGTE unary data (Dinsdale 1991), but many important binaries have been assessed several times using different models for some of the phases, which are not always compatible. When selecting which assessed version of a system should be incorporated into a database, the thermodynamic description should, at least ideally, be the best that can be obtained at present, taking into account theoretical approaches and technical possibilities. Of course, what should be judged the “best” assessment is not easy to define, but some rules can be established, as will be discussed in this book.

A series of thermodynamic and modeling workshops organized by the Max Planck Institute in Stuttgart and held in the conference center at Schloss Ringberg was initiated in 1995. The aim of these workshops was to build the foundation for the next generation of thermodynamic databases and software. They had a unique organization with from five to seven groups, with from seven to nine participants in each. The participants in each of the groups were expected to write a paper together on a specific topic during the workshop, with some time to complete it allowed afterwards. The participants had quite different opinions initially, but during the workshop many new ideas on how to resolve the differences or find ways to resolve them appeared. The first workshop was dedicated to pure elements and compounds and was published as a special issue of *Calphad* (Aldinger *et al.* 1995). The second workshop was dedicated to modeling of solutions and was published in *Calphad* (Aldinger *et al.* 1997). The third was dedicated to applications and published in *Calphad* (Aldinger *et al.* 2000) and the *Zeitschrift für Metallkunde* (Burton *et al.* 2001). The fourth was about applications and modeling of special phases such as oxides and was also published in the *Zeitschrift für Metallkunde* (Aldinger *et al.* 2001). The fifth workshop was about Calphad and *ab initio* techniques and was published in *Calphad* (Aldinger *et al.* 2007).

1.4 The structure of the book

This book is intended to be an introductory text as well as a reference book for optimization of thermodynamic descriptions, but it is not intended to be read from beginning to end. This first chapter gives some introduction to the scope of the book. The second chapter is

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for reference, since its content should be well known to any student of physics, chemistry, or materials science, and the notation for thermodynamic quantities used in the book is explained.

Chapter 3 gives a short introduction to *ab initio* calculations, in particular how results from such calculations can be used for thermodynamic modeling and assessments. In the fourth chapter various experimental techniques that provide the data necessary for assessments are described. The fifth chapter gives a detailed description of most of the models currently used to describe thermodynamic functions of phases. This is mainly intended to be a reference for the sixth chapter, where the selection of models for phases is discussed in terms of their properties.

Chapter 6 is the central part of the book, where the experience from many assessments has been condensed into a few rules of practice. As usual, any good rule has many exceptions; many of these exceptions will be described in chapter 9, which deals with case studies. The reader may find that some topics are repeated several times; that is usually because they are important.

Chapter 7 describes two of the most-used software systems for thermodynamic assessments, BINGSS, developed by H. L. Lukas (Lukas *et al.* 1977, Lukas and Fries 1992) and PARROT, developed by Dr. B. Jansson (Jansson 1983) as a part of the Thermo-Calc software (Sundman *et al.* 1985, Andersson *et al.* 2002). The emphasis is on the main features of these items of software; many of the peculiarities will be explained only in the case studies in chapter 9. Chapter 8 deals with the creation of databases from separate assessments and how to maintain a database.

Chapter 9 is again a crucial part of the book. The beginner should try to follow some of the case studies in order to learn the technique from a known system. A careful reading of the case studies is recommended, since they give many hints on how to use experimental data of various types. The reader is also advised to look at the website for the book, because more case studies will be available there. References to existing software and databases can be found in a special issue of *Calphad* (2002, **26**, pp. 141–312).

2 Basis

2.1 Thermodynamics

A short overview on the rules of thermodynamics shall be given here, with special emphasis on their consequences for computer calculations. This part will not replace a textbook on thermodynamics, but shall help the reader to remember its rules and maybe present them in a more practically useful way, which facilitates the understanding of thermodynamic calculations.

Thermodynamics deals with energy and the transformation of energy in various ways. In thermodynamics all rules are deduced from three principal laws, two of which are based on axioms expressing everyday experiences. Even though these laws are very simple, they have many important consequences.

Thermodynamics can strictly be applied only to systems that are at equilibrium, i.e. in a state that does not change with time. As noted in the introduction, the thermodynamic models can be extrapolated outside the equilibrium state and provide essential information on thermodynamic quantities for simulations of time-dependent transformations of systems.

2.1.1 The equation of state

The concept of thermodynamic state must be introduced before beginning with the principal laws. This can be done by invoking the principle of the “equation of state.” This is connected with the introduction of temperature as a measurable quantity. If pressure–volume work is the only work considered, then one can state that *in a homogeneous unary system the state is defined by two variables*. Of the three variables temperature T , pressure p , and volume V in a unary system, only two are independent, i.e. there exists a condition

$$F(T, p, V) = 0 \quad (2.1)$$

which means that one of the three variables is determined by the other two:

$$V = f(T, p); \quad T = f(V, p); \quad \text{or} \quad p = f(T, V) \quad (2.2)$$

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A unary system consists of a single component, either an element from the periodic table or a molecule that will not form any other molecules under the conditions considered. For the definitions of the terms “homogeneous,” “system,” etc., any general textbook on thermodynamics, for example Hillert *et al.* (1998), can be consulted.

For each additional kind of work considered, e.g. magnetic or electric, an additional variable is necessary to define the state. Nevertheless, the above consideration is very useful and, if the pressure dependence can be neglected, the state functions of pure substances (unary phases) are functions of the temperature only.

For practical reasons a “state” may be defined for inhomogeneous systems, but that can be taken as a simplified notation for the sum or integral of (eventually infinitesimally small) homogeneous systems, for each of which the state has to be defined separately.

To define the state of non-unary (binary, ternary, . . .) systems, one needs additional variables, for example the amounts of the components. These may be replaced by mole- or mass-fractions together with the total amount.

2.1.2 The first law of thermodynamics

This law is derived from the axiom of conservation of energy. A formulation well suited for our purpose is the following: *the sum of the heat and work transferred to an otherwise closed system defines a function not depending on the way in which this transfer took place.* The function defined in this way is called the internal energy U . A “closed system” means a system that does not exchange any heat, work, or matter with its surrounding. Besides constant internal energy U , it has constant volume V and a constant amount of matter (expressed as constant amounts N_i of different components i). All these quantities depend only on the “state” of the system and they are called state variables or state functions. The concept of state functions is very important in thermodynamics. A feature of the internal energy U , which must be kept in mind for numerical calculations, is that only differences between the values of this function for two well-defined states have a physical meaning. No absolute value of U can be defined.

If the system is opened and either *heat*, q , or *work*, w , is transferred to it from the surroundings, the above rule can be formulated in terms of a change of the internal energy:

$$\Delta U = q + w \quad (2.3)$$

Neither q nor w is itself a state variable. Transferring either only heat or only work may be different ways of bringing about the same change of state.

2.1.3 The second law of thermodynamics

This law is derived from the axiom that a complete conversion of heat to work is not possible. It may be formulated as follows: *a function of state, called entropy and denoted S , can be defined, which can increase, but never decrease, in a closed system.* The state

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in which the entropy of the closed system has its maximum is the equilibrium state. No further change of state can happen in this system as long as it remains closed.

The difference between the entropies of two well-defined states of a system (that is not closed) is defined by the integral

$$S_2 - S_1 = \int_{\text{state 1}}^{\text{state 2}} \left(\frac{dQ}{T} \right)_{\text{rev}} \quad (2.4)$$

dQ is the infinitesimal amount of heat transferred to the system on the way from state 1 to state 2. The subscript “rev” indicates that the path from state 1 to state 2 must be reversible, which means that it is restricted to a sequence of equilibrium states. On going in non-reversible ways from state 1 to state 2, some work is added instead of heat. All real changes of state are irreversible, but a reversible change of state may be simulated by a *Gedankenexperiment*, i.e., an experiment that one may think of doing, but which it is impossible to do in reality.

2.1.4 The third law of thermodynamics

This law is derived from the axiom that it is impossible to reach the temperature of 0 K. This temperature can be approached only asymptotically. A consequence of this axiom is that *the change in entropy of a reversible reaction approaches 0 when the reaction temperature approaches 0 K*. By virtue of this law an absolute value can be defined for the state function entropy, S , in contrast to the internal energy U . By convention S is set to zero at 0 K.

2.1.5 Definition of some terms and symbols

A number of symbols will be used and the most important are summarized here. In most cases they refer to just one phase. Whenever more than one phase is involved, a superscript like α or β will be used to distinguish the phases involved. A superscript tot will be used when it is emphasized that the symbol refers to the total value for the system, summed over all phases. A phase is distinguished by its crystal structure (see section 2.2), and at equilibrium its composition is homogeneous in space. The gas, liquid, and the amorphous or glass phase are also phases, even though they have no crystal structure. Names of phases are discussed in section 8.4.

The term “constituent” means any species that can be treated as an independent entity to describe the constitution of a phase, for example molecules in a gas or a defect in a crystalline phase; see section 5.3.

- T the absolute temperature.
- R the gas constant, $8.31451 \text{ J mol}^{-1} \text{ K}^{-1}$.
- p the pressure.
- V the volume.
- Q the heat.
- N_i the number of moles of component i .

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- N the total number of moles, $N = \sum_{i=1}^n N_i$.
 N_A Avogadro's number, 6.023×10^{23} atoms per mole.
 x_i the mole fraction of component i , $x_i = N_i/N$.
 y_i the fraction of constituent i . The sum of the constituent fractions is unity; however, since y_i depends on the solution model for the phase, there may be more constituents than components, with the consequence that there is no general relation between the constituent fractions and the mole fractions.
 Y short for denoting the constitution, i.e., all constituent fractions in a phase.
 G the total Gibbs energy of a system.
 G_m the Gibbs energy per mole of components of a system.
 G_m^θ the Gibbs energy per mole of components of phase θ .
 G_i^θ the partial Gibbs energy of component i in phase θ .
 ${}^\circ G_i^\theta$ the Gibbs energy for the pure component i in phase θ .
 μ_i the chemical potential of component i .
 a_i the activity of component i , $a_i = \exp[\mu_i/(RT)]$.

There are often several specifications to these symbols placed as superscripts and subscripts. The superscript is reserved for the phase, power, or sublattice indication. As subscript one can have the normalization "m" or the specification of a component or other things. The "pre"-superscript is used to specify that the symbol is for a pure element, "°", an excess quantity "E" or anything else that does not fit as a subscript.

2.1.6 Equilibrium conditions and characteristic features

A first condition of equilibrium is that all parts of a system have the same temperature and the same pressure. Inhomogeneities at equilibrium may occur only on having different "phases," each of which, however, must be homogeneous in itself. This is a direct consequence of the second law. A system with a temperature gradient may be simplified by dividing it into hotter and colder parts. By transferring heat from a hotter part to a colder part, according to Eq. (2.4) the entropy loss in the hotter part is less than the entropy gain in the colder part, and thus the total entropy of the system is increased. Similarly, equilibration of composition gradients increases entropy. This can be shown by "van 't Hoff's equilibrium box," as is explained in most textbooks on thermodynamics.

Experimentally, pressure differences can be maintained for quasi-infinite times and thus equilibrium with different pressures inside a system would seem possible. However, such a pressure barrier means that the system is divided into parts forming independent closed systems. Considering it as a single closed system implies that the pressure barrier can be opened.

Systems in equilibrium have single scalar values for temperature and pressure, the temperature and pressure of the system. A general system, in contrast, may have a temperature and a pressure field, i.e., temperature and pressure may vary with coordinates in space and the expression "temperature of the system" would be meaningless.