

4. Thermodynamics

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4.1. Overview

Thermodynamic modelling is software that uses thermodynamic calculations to predict the properties and behaviours of materials under various conditions. At its most basic, for example, thermodynamic modelling software provides information such as the melting point of an alloy, but in practice, the software is used to answer much more complicated and time-consuming questions about the behaviour of complex materials.

Thermodynamic modelling is currently one of the most mature areas of ICME (Integrated Computational Materials Engineering), and companies that produce software tools for thermodynamic modelling are deeply involved in initiatives in the EU and US to advance the ICME vision, so thermodynamic modelling will likely continue to be an important part of many ICME projects.

This chapter gives an overview of the current theory and practice of thermodynamic modelling. Sections 4.2 and 4.3 provide an introduction to some basic thermodynamic concepts and theory. Section 4.4 then gives an overview of the so-called CALPHAD (CALculation of Phase Diagrams) method, which is a thermodynamic modelling approach frequently used when it comes to solving practical material design problems that involve multi-component systems. In this approach, thermodynamic calculations provide the information on phases in stable or metastable equilibrium that are needed for predicting properties of materials under a wide range of temperature, pressure and composition conditions.

Section 4.5 focuses on thermodynamic data, data formats and databases. The following section, 4.6, is concerned with how thermodynamic data and modelling can be integrated with modelling at larger scales. Section 4.7 then provides a set of examples of how thermodynamic modelling has been successfully used in various research and engineering projects. Section 4.8 contains a table of software tools and applications available for thermodynamic modelling, and the chapter concludes in section 4.9 with a list of recommended further reading.

4.2. Basic concepts and principles

In thermodynamics, reality is simplified to the extent possible without sacrificing information about the static properties of the system. Thermodynamics builds on a *system* that is fully represented by a finite set of scalar, or sometimes tensorial, *state* variables. While these systems are adequate to describe the static properties of most solids, liquids and gases, it is not a fully dynamic model and, therefore, has limitations, e.g. natural fluctuations occurring within the system are not covered by the theory. A thermodynamic system has two extremes of complexity: *general* and *simple*. A *general* system description must aptly characterize micro- and nanostructures, anisotropic properties and

tensorial stress components, and maybe interaction with external fields; whereas a *simple* system, which is uniform throughout, is described by scalar state variables only, and does not interact with external fields. In this chapter, the discussion will be limited to simple systems.

A thermodynamic system is composed of the matter within a set space. Around the system is a *boundary*, or wall, and beyond that is everything else in the universe, known as the *surroundings*. An *open* system is one in which the system exchanges matter with its surroundings. By contrast, a *closed* system does not exchange matter with its surroundings. Taken further, an *isolated* system exchanges neither matter nor energy. For practical reasons the *closed* system is very important in the thermodynamics of material sciences. Note that the term control volume in fluid mechanics is often used synonymously with an *open* system in thermodynamics. The boundary is then called a control surface. An *adiabatic* boundary is in this respect equivalent to a perfect insulator, and a *diabatic* boundary is equivalent to a perfect heat conductor.

These are the main elements of the language used to underpin thermodynamic analyses of real-world systems. The dualism between the physical reality on the one side, and abstract thermodynamic analysis on the other side, is always at the centre.

4.2.1. The concept of the thermodynamic state

The *state* of a thermodynamic system is determined by the system's properties—and vice versa. A *property* is here taken to be a state variable that is independent of the past, known as the history or the *path* of the system. It is the current state of the system that matters. The logic is seemingly circular, but from an experimental point of view the state is defined if, or when, all the independent thermodynamic properties have been measured.

In doing measurements, we often distinguish between *extensive* and *intensive* state properties. These terms relate to properties that, respectively, depend on the size of the system and those that are size independent. It is also common to distinguish between *external* state variables controlled by the experimentalist and *internal* state variables that are unattainable from the outside but still influenced by the external state variables and having well defined values at equilibrium (explained later in this section).

One aid in revealing the properties of the system is the *process*, which is used to describe the changes that take place along a given path from one state to another. Hence, the path contains a complete description of the history of the process, or the sequence of state changes, if you like. A physical state change always implies the action of time, and the path is inherently time-dependent, but for a *stationary* process the state is time invariant and the path is reduced to a static step change from the input state to the output state. The same simplification applies to a process that has an indefinite time at its disposal. In this case the state will approach its *equilibrium* value, which is the foundation of all the thermodynamic analysis laid out in this chapter. We shall see later that the energy of the system is being minimised in this particular state.

The number of state variables for a simple system is not universally fixed. In the simplest case there are $C + 2$ such variables, where C is the number of independent chemical components (typically atoms) and the number 2 represents temperature and pressure. The practical application determines the number of chemical composition variables involved. Distilled water can e.g. be described using a single chemical component called H_2O under normal conditions, or using 5 components involving 9 different chemical constituents in an isotope enrichment plant. Taking H_2 and O_2 into account, or

perhaps H_3O^+ and OH^- , does not increase the degrees of freedom insofar as the overall stoichiometry of the system is equal to H_2O .

4.2.2. Fundamental relations and canonical state variables

Thermodynamics is a phenomenological science, which means it is not supported by any strong theories of its own. Its foundation rests on numerous experimental facts forming a set of principles guiding our understanding on how to view a thermodynamic system. In the mid eighteenth century there was an increasing body of observations indicating that a change in the internal energy of a closed system is the difference of two actions (non-exact differentials) called heat and work:

$$dU_{c-s} = \delta Q - \delta W.$$

This is known as the first law of thermodynamics, which states that the internal energy of a closed system does not change unless there is an interaction with the outside environment. At about the same time it was also recognized that, for so-called *reversible* state changes of simple systems, p and T serve as integrating factors for δW and δQ , turning the non-exact differentials into exact ones:

$$\begin{aligned}\delta W_{\text{rev}} &= p dV, \\ \delta Q_{\text{rev}} &= T dS.\end{aligned}$$

The last of these relations is known as the second law of thermodynamics. Around 1873 Gibbs topped the knowledge with an exact understanding of open systems:

$$dU = T dS - p dV + \sum_i \mu_i dN_i.$$

He also recognized that U is a state function in S , V and N_i . As a consequence the differential is valid for all state changes, not only the reversible ones, given that the start and end points are equilibrium states. At the end of the century, it became clear that S is not only a state function but that it also has a definite zero, making it possible to integrate the differential into a *fundamental* form:

$$U = TS - pV + \sum_i \mu_i N_i.$$

The integrated form of U is known as an Euler homogeneous function of order one, and S , V and N_i as the *canonical* variables of U . The factors T , p and μ_i do not have clear-cut names but we might refer to them as the thermal, mechanical and chemical potentials of the system. Grouped together, TS , pV and $\mu_i N_i$ are often called *conjugated* pairs of variables. In thermodynamics we also refer to canonical potentials, meaning those that contain all thermodynamic information about the system. From applying Legendre transformations to internal energy we can prove the existence of eight canonical energy potentials. The definition of the Legendre transformation ϕ of an arbitrary function f is rather simple:

$$\text{Eq. -4.1} \quad \phi(\xi_i, x_j, x_k, \dots, x_n) \equiv f(x_i, x_j, x_k, \dots, x_n) - \left(\frac{\partial f}{\partial x_i} \right)_{x_j, x_k, \dots, x_n} x_i.$$

But applied to internal energy U we get seven functions of general interest: Helmholtz energy A , enthalpy H , Gibbs energy G , grand canonical potential Ω , zero potential O and two unnamed

potentials given the symbols X and Y . An interesting property of the Legendre transform is that if we know one potential we know them all. This is not trivial as, for instance, $U(T, V, \mathbf{n})$ and $H(T, -p, \mathbf{n})$ do not have this property. For a thermodynamic function with $m = \dim(\mathbf{n}) + 2$ variables there are $2^m - 1$ Legendre transforms. For a single-component system this means that there are $2^3 - 1 = 7$ possibilities. By using Eq. -4.1 on each of the variables in turn we get three of the transforms:

$$\begin{aligned}
 A(\tau, V, N) &= U(S, V, N) - \left(\frac{\partial U}{\partial S}\right)_{V,N} S \equiv U - \tau S, \\
 H(S, \pi, N) &= U(S, V, N) - \left(\frac{\partial U}{\partial V}\right)_{S,N} V \equiv U - \pi V, \\
 X(S, V, \mu) &= U(S, V, N) - \left(\frac{\partial U}{\partial N}\right)_{S,V} N \equiv U - \mu N.
 \end{aligned}$$

Eq. -4.2

By using Eq. -4.1 on pairs of two variables we can obtain three more transforms:

$$\begin{aligned}
 G(\tau, \pi, N) &\equiv U - \pi V - \tau S, \\
 Y(S, \pi, \mu) &\equiv U - \pi V - \mu N, \\
 \Omega(\tau, V, \mu) &\equiv U - \tau S - \mu N.
 \end{aligned}$$

Eq. -4.3

Finally, by using Eq. -4.1 on all three variables in succession we can obtain the null potential $O(\tau, \pi, \mu) \equiv U - \pi V - \tau S - \mu N$, but strictly speaking it is yet to be explained why this result requires that U is Euler homogeneous.

By examining the results carefully we can prove that repeated Legendre transformation defines a closed algebraic loop, wherein the original information contained in U is retained, as shown below:

$$\begin{array}{ccc}
 U(S, V, N) & \xrightarrow{S} & A(\tau, V, N) \\
 \uparrow -\tau & & \downarrow \tau \\
 A(-\tau, V, N) & \xleftarrow{-S} & U(-S, V, N)
 \end{array}$$

This cycle represents, so to speak, the Pandora's box of thermodynamics: from it, an infinite palette of interconnected relations spring out — to the great dismay of many a student of physics, chemistry and metallurgy. At this point, a second property of the thermodynamic potential comes to our rescue, namely the Euler homogeneity of order one.

Generally speaking, a stand-alone hypothesis in thermodynamics claims that the energy of a system is written

$$U = \left(\frac{\partial U}{\partial X_1}\right) X_1 + \left(\frac{\partial U}{\partial X_2}\right) X_2 + \cdots + \left(\frac{\partial U}{\partial X_n}\right) X_n$$

provided all the *extensive* state variables X_i , and all the *intensive* properties $(\partial U/\partial X_i)$, are known. It turns out that the difference between the extensive and the intensive functions fits into a more general classification scheme. They are, respectively, Euler homogeneous functions of order one and order zero. More precisely, the function $f(x_1, \dots, x_n, \xi_{n+1}, \dots, \xi_m)$ is homogeneous of order k in the variables x_1, \dots, x_n if the following criteria are satisfied:

$$\begin{aligned}
 F(X_1, \dots, X_n, \xi_{n+1}, \dots, \xi_m) &= \lambda^k f(x_1, \dots, x_n, \xi_{n+1}, \dots, \xi_m), \\
 X_i &\equiv \lambda x_i.
 \end{aligned}$$

Eq. -4.4

This scaling law is known as Euler homogeneity of the order k . A mathematical analysis of Eq. -4.4 reveals several interesting results, of which we are going to mention only one:

$$\text{Eq. -4.5} \quad \sum_{i=1}^n X_i \left(\frac{\partial F}{\partial X_i} \right)_{X_{j \neq i} \xi_i} = kF.$$

Applying Eq. -4.5 to Eq. -4.2, and to Eq. -4.3, yields a table of Legendre–Euler equivalents of internal energy (restricted to a single component system below). The Euler form is in each case equivalent to the Legendre transform bearing the same function name, even though their functional forms look totally different:

Table 4.1: Euler integral forms of Legendre transformed internal energy.

Function	Variables	Derivatives	Euler form	Legendre form
U	S, V, N	τ, π, μ	$\tau S + \pi V + \mu N$	U
A	τ, V, N	$-S, \pi, \mu$	$\pi V + \mu N$	$U - \tau S$
H	S, π, N	$\tau, -V, \mu$	$\tau S + \mu N$	$U - \pi V$
X	S, V, μ	$\tau, \pi, -N$	$\tau S + \pi V$	$U - \mu N$
G	τ, π, N	$-S, -V, \mu$	μN	$U - \tau S - \pi V$
Ω	τ, V, μ	$-S, \pi, -N$	πV	$U - \tau S - \mu N$
Y	S, π, μ	$\tau, -V, -N$	τS	$U - \pi V - \mu N$
O	τ, π, μ	$-S, -V, -N$		$U - \tau S - \pi V - \mu N$

In the table we have used $\pi \equiv -p$ in order to provide a consistent rule for the sign shifts of the derivatives: the derivative taken with respect to a transformed variable is always the negative of the untransformed variable.

4.2.3. Equations of state (EOS)

To describe the thermodynamic state we need one or more functions that define the asymptotic behaviour of the system (say a chemical mixture) in a consistent manner. Applying parameters to the functions renders flexibility to the engineer, while the asymptotes guarantee thermodynamic consistency. In this section we will have a brief look at a variety of useful concepts, such as ideal gas, virial expansion, the Debye phonon model and Van der Waals theory, but first we need to define the concept of an equation of state. Let us start with the differential of a known thermodynamic potential. E.g. internal energy has

$$\text{Eq. -4.6} \quad dU = TdS - pdV + \sum_{i=1}^n \mu_i dN_i,$$

in terms of the canonical variables S, V and N_i . Now, if we know the fundamental state functions referred to as the *equations of state* of the system:

$$\text{Eq. -4.7} \quad \begin{aligned} T &= T(S, V, \mathbf{n}), \\ p &= p(S, V, \mathbf{n}), \\ \mu_i &= \mu_i(S, V, \mathbf{n}), \end{aligned}$$

then Eq. -4.6 can be integrated using Euler's first theorem in Eq. -4.5 to give $U = TS - pV + \sum_{i=1}^n \mu_i N_i$. However, this will not work in practice because the equations of state in Eq. -4.7 rarely exist as explicit relations (for a photon gas it will). In practical work, it is therefore more convenient to start with

$$(dG)_{T,p} = \sum_{i=1}^n \mu_i dN_i,$$

or, alternatively

$$(dA)_T = -pdV + \sum_{i=1}^n \mu_i dN_i,$$

which can be integrated once $\mu_i(T, p, \mathbf{n})$, or, alternatively, $p(T, V, \mathbf{n})$ and $\mu_i(T, V, \mathbf{n})$, are known to us. By taking the ideal gas model as a reference, it is possible to obtain the residual functions $G^{r,p}$ and $A^{r,v}$ described in Section 4.3.1. From these we can derive the Gibbs or Helmholtz energy of the mixture, and a consistent set of state functions can then be *derived* using partial differentiation.

Perfect gas

The partition function for a particle-in-box without vibrational or rotational degrees of freedom yields the following set of canonical equations of state for Helmholtz energy:

Eq. -4.8

$$\frac{p^{\text{trans}} V}{NRT} = 1,$$

$$\frac{\mu^{\text{trans}}}{RT} = -\frac{3}{2} \ln \left[\frac{2\pi M_w RT}{N_A^2 h^2} \left(\frac{V}{NN_A} \right)^{2/3} \right].$$

Harmonic oscillator

The atoms in a molecule are held together by forces which, for small perturbations, allow the atoms to vibrate as if their centres were connected by elastic springs. The partition function for a *harmonic* oscillator of this kind having a characteristic frequency ν , quantum number j and energy factor $\varepsilon = h\nu = \hbar\omega/2\pi \equiv \hbar\omega$, yields

$$\frac{\mu^{\text{vib}}}{RT} = \ln \left[2 \sinh \left(\frac{\hbar\omega}{2kT} \right) \right].$$

Vibrations in crystals

For vibrations in a crystal lattice, Einstein assumed that all atoms vibrate independently with the same frequency in all directions. Vibrations in three spatial directions simultaneously is easily accounted for by multiplying μ^{vib} and c_v^{vib} given above with a factor 3. More realistically, the distribution of the frequencies of vibration is a function of the frequency itself. Debye assumed that the distribution is proportional to ω^2 up to ω_{max} . This gives rise to the formula

$$\frac{\mu^{\text{Debye}}}{RT} = 9 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} x^2 \ln(1 - e^{-x}) dx,$$

where $\theta_D \equiv \hbar\omega_{\text{max}}/k$ is the so-called Debye vibrational temperature.

Virial expansion of gases

The virial expansion relates to thin gases. There is also an equivalent power series expansion for osmotic pressure in dilute solutions. Expanding p/RT in molar density $\rho = N/V$ yields

$$\text{Eq. -4.9} \quad \frac{p^{\text{vir}}V}{NRT} = \sum_{k=1}^{\infty} B_k(T) \left(\frac{N}{V}\right)^{k-1} = 1 + B_2(T) \frac{N}{V} + \dots$$

This is the normal way to express the virial expansion of gases. The series converges rapidly at low density, but not at higher i.e. liquid-like densities. Thus, for the study of vapor–liquid equilibria we need a more versatile equation of state described in the next section.

Van der Waals fluid

For a given vector \mathbf{n} consisting of the mole numbers N_1, N_2, \dots, N_n the Van der Waals equation of state can be expressed as

$$\text{Eq. -4.10} \quad p^{\text{vdW}} = \frac{NRT}{V - B(\mathbf{n})} - \frac{A(\mathbf{n})}{V^2},$$

where $A(\mathbf{n})$ tells us something about the *attractive* forces between the molecules and $B(\mathbf{n})$ represents the *hard-sphere* volume of the mixture. By expanding Eq. -4.10 in the ideal gas limit $V \rightarrow \infty$ and comparing the coefficients with the ones in Eq. -4.9, we find that $B_2^{\text{vdW}} = b - a/RT$, $B_3^{\text{vdW}} = b^2$, $B_4^{\text{vdW}} = b^3$, etc. Only B_2^{vdW} resembles the behaviour of a real gas; the other coefficients are unrealistic. Even so, the Van der Waals equation of state is our simplest starting point for equations that are going to model phase condensation phenomena.

4.2.4. Euler integration of EOS into a fundamental relation

The first challenge is to generalise the ideal gas law in Eq. -4.8 into one that is similarly valid for a multicomponent system. In order to do that, we must write the ideal gas law in its extended form

$$\text{Eq. -4.111} \quad p^{\text{ig}} = \sum_i \frac{N_i RT}{V},$$

so that we can identify the components that constitute the mixture. It is an equation of state in the form $p(T, V, \mathbf{n})$, which eventually leads to Helmholtz energy $A(T, V, \mathbf{n})$, but in order to use the Euler method of integration in Eq. -4.5, we also need to know the equation of state $\mu_i^{\text{ig}}(T, V, \mathbf{n})$. This function cannot be obtained experimentally in the same way as p^{ig} , and must therefore be derived theoretically. The normal convention is to assume the pure component standard state $V_o/N_i^o = RT/p_o$ where $p_o = 1\text{bar}$. Referring to $\mu_i^o(T, p_o)$ as the standard state, the chemical potential of component i can be expressed as

$$\text{Eq. -4.12} \quad \mu_i^{\text{ig}}(T, V, \mathbf{n}) = \mu_i^o(T, p_o) + RT \ln \left(\frac{N_i RT}{p_o V} \right).$$

Compared to the monoatomic potential in Eq. -4.8, this equation has a more general temperature dependency; it also relates to a multiple of components $i \in [1, n]$ and to the standard pressure p_o . It is now worth reiterating that using Euler's theorem to integrate Eq. -4.11 and Eq. -4.12 always works, and that the Helmholtz energy of the gas can be expressed in the following general form:

$$A^{ig}(T, V, \mathbf{n}) = \pi^{ig}V + \sum_i N_i \mu_i^{ig} = - \sum_i N_i RT + \sum_i \frac{N_i \mu_i^\circ(T, p_o)}{c^\circ(T, p_o, \mathbf{n})} + \sum_i N_i RT \ln \left(\frac{N_i RT}{p_{ov}} \right)$$

Note that the standard state is based on a conventional Gibbs energy function, because T and p_o have been selected as the state variables of μ_i° , rather than T and V_o . The calculation of $\mu_i^\circ(T, p_o)$ is normally done in terms of a heat capacity integral:

$$\mu_i^\circ(T, p_o) = \Delta_f h_i^\circ + \int_{T_o}^T c_{p,i}^\circ(\tau) d\tau - T \left[s_i^\circ(T_o, p_o) + \int_{T_o}^T \frac{c_{p,i}^\circ(\tau)}{\tau} d\tau \right],$$

$$c_{p,i}^\circ = R + c_{v,i}^{\text{trans}} + c_{v,i}^{\text{rot}} + \sum c_{v,i}^{\text{vib}} + \dots$$

Condensed phases, and complex gaseous phases, are not readily applicable to a quantum mechanical description and do therefore rely on empirical correlations for $c_{p,i}^\circ$. Even polynomial formulas are used for this purpose, but that practice is questionable because polynomials will eventually diverge at high temperatures.

4.2.5. The principle of thermodynamic equilibrium

In a physical system the *external* state variables define a differentiable manifold on which a particular function of the state (yet to be defined) varies in terms of the *internal* state variables such that it eventually reaches a time invariant state called the equilibrium state. An alternative view of the physical picture is that the same function is allowed to vary with respect to all the state variables subject to a set of extensive *constraints*. The first view represents a generalization of the *extent of reaction* known from physical chemistry, whilst the latter leans towards the method of unknown Lagrange *multipliers* in optimisation theory. The last one is the line of thought followed in this text.

Take it for granted, therefore, that the state is properly defined as a set of extensive variables making up one of the canonical potentials from the last section. Applied to a simple system, where each chemical component $i \in [1, n]$ is present in every phase $\pi \in [\alpha, \omega]$, the stationary conditions are equivalent to a spatial uniformity of T , p and μ_i in the system. We shall now prove that these conditions are equivalent to minimising the internal energy for a given total entropy, volume and mole numbers:

$$U_{\text{eq}} = \min_{\forall \mathbf{x}^{(\pi)}} U(\mathbf{x}^{(\alpha)}, \mathbf{x}^{(\beta)}, \dots, \mathbf{x}^{(\omega)}),$$

subject to:

$$\mathbf{x}^{(\alpha)} + \mathbf{x}^{(\beta)} + \dots + \mathbf{x}^{(\omega)} = \mathbf{x}_o.$$

Eq. -4.13

Here, $\mathbf{x}^{(\pi)} \equiv (S^\pi \quad V^\pi \quad N_1^\pi \quad \dots \quad N_n^\pi)$ is a list of extensive state variables for the arbitrary phase π . In all stationary states the differential of U must vanish for all *feasible* variations in S^π , V^π and N_i^π :

$$(dU)_{S,V,\mathbf{n}} = \sum_{\pi=\alpha}^{\omega} dU^\pi = \sum_{\pi=\alpha}^{\omega} (T^\pi dS^\pi - p^\pi dV^\pi + \sum_{i=1}^n \mu_i^\pi dN_i^\pi) = 0.$$

From these $n + 2$ balance equations we can eliminate dS^ω , dV^ω and dN_i^ω for all the components $i \in [1, n]$. Substituted into the differential of U :

$$(dU)_{S,V,\mathbf{n}} = \sum_{\pi=\alpha}^{\omega-1} [(T^\pi - T^\omega) dS^\pi - (p^\pi - p^\omega) dV^\pi + \sum_{i=1}^n (\mu_i^\pi - \mu_i^\omega) dN_i^\pi] = 0.$$

In the neighbourhood of an equilibrium point, the quantities $dS^\alpha, \dots, dS^{\omega-1}$ and $dV^\alpha, \dots, dV^{\omega-1}$ and $dN_\alpha^1, \dots, dN_n^{\omega-1}$ are truly independent, thus representing the internal state variables mentioned in the beginning of this section. If $(dU)_{S,V,n} = 0$ then it must be true that:

$$\begin{aligned} T^\alpha &= T^\beta = \dots = T^\omega, \\ p^\alpha &= p^\beta = \dots = p^\omega, \\ \mu_1^\alpha &= \mu_1^\beta = \dots = \mu_1^\omega, \\ &\vdots \\ \mu_n^\alpha &= \mu_n^\beta = \dots = \mu_n^\omega. \end{aligned}$$

When relating these results with the differentials of Eq. -4.2 and Eq. -4.3 it dawns on us that the exact same equilibrium conditions are reached by minimizing any of the potentials with only slight changes to the constraints:

$$\min_{S,V,n} U \Leftrightarrow \min_{S,n} (H)_p \Leftrightarrow \min_{V,n} (A)_T \Leftrightarrow \min_n (G)_{T,p} \Leftrightarrow \dots \Leftrightarrow \min_v (\Omega)_{T,\mu}.$$

Minimising internal energy with respect to entropy, volume and mole numbers is therefore equivalent to minimising Helmholtz energy at given T with respect to both volume *and* mole numbers, or Gibbs energy at given T and p with respect to the mole numbers *only*. All the equations we have seen so far are valid for the generic phase equilibria problem but we would also like to know how to solve heterogeneous reaction equilibria. In order to achieve this major change in the system description we only need to change the constraint specification, from the form

$$\mathbf{x}^{(\alpha)} + \mathbf{x}^{(\beta)} + \dots + \mathbf{x}^{(\omega)} = \mathbf{x}_0$$

which is used in Eq. -4.13, to

$$\mathbf{B}^{(\alpha)} \mathbf{x}^{(\alpha)} + \mathbf{B}^{(\beta)} \mathbf{x}^{(\beta)} + \dots + \mathbf{B}^{(\omega)} \mathbf{x}^{(\omega)} = \mathbf{x}_0$$

where $\mathbf{B}^{(\alpha)}, \mathbf{B}^{(\beta)}$, etc. are constant (albeit phase specific) constraint matrices. In ordinary phase equilibria $\mathbf{B}^{(\pi)} = \mathbf{I}$ for all $\pi \in [\alpha, \omega]$. In many heterogeneous systems involving molten metals, ceramic phases at high temperatures, aqueous electrolytes and other fully dissociated system, the formula matrices takes the more general form

$$\mathbf{B} = \begin{pmatrix} \mathbf{I}_{2 \times 2} & 0 \\ 0 & \mathbf{A}_{m \times n} \end{pmatrix},$$

where \mathbf{A} is the atoms \times substance matrix and \mathbf{I} corresponds with constraints in S and V . By substituting the new constraint formulation into Eq. -4.13 there is a new set of more general equilibrium conditions. That is to say, the thermal and mechanical equilibria are unchanged but the chemical equilibrium is changed into

$$\mu^\alpha = \mathbf{A}^\alpha \lambda, \quad \mu^\beta = \mathbf{A}^\beta \lambda, \quad \dots, \quad \mu^\omega = \mathbf{A}^\omega \lambda,$$

where λ is a vector of Lagrange multipliers associated with the problem. For kinetically hindered reactions \mathbf{A} is not the atoms \times substance matrix anymore. We should then think of the matrix as spanning the null space of the reaction stoichiometry matrix \mathbf{N} . The constraint situation does not change, however, and the equilibrium conditions are also unchanged if $\mathbf{A} \equiv \text{null}(\mathbf{N}^T)$ such that $\mathbf{A}\mathbf{N} = 0$. About the role of \mathbf{A} and \mathbf{N} we should make the comment that minimising U with respect to

$\mathbf{x}^{(\pi)}$ in the row space of $\mathbf{B}^{(\pi)}$ calls for the use of Lagrange multipliers, whilst minimising U in the column space of \mathbf{N} leads to a generalization of the concept of extents of reactions.

4.3. Thermodynamic modelling

The ideal gas serves as the theoretical limit for all real fluids, but for solid solutions and complex liquids there are other kinds of ideality. That is to say, an ideal molecular mixture is similar to an ideal gas mixture at a fixed pressure, while e.g. an ionic liquid behaves closer to the so-called Temkin model where the cations and the anions mix on two separate sublattices. A similar concept also applies to solid solutions, but the number of possible spatial arrangements is not so obvious in this case. It is therefore customary to reserve the Gibbs and Helmholtz residual functions

$$\begin{aligned} G(T, p, \mathbf{n}) &= G^{\text{ig}}(T, p, \mathbf{n}) + G^{\text{r,p}}(T, p, \mathbf{n}), \\ A(T, V, \mathbf{n}) &= A^{\text{ig}}(T, V, \mathbf{n}) + A^{\text{r,v}}(T, V, \mathbf{n}), \end{aligned}$$

to fluids, while solid solutions and complex liquids are better served by an excess Gibbs energy function:

$$G(T, p, \mathbf{n}) = G^{\text{id}}(T, p, \mathbf{n}) + G^{\text{ex}}(T, p, \mathbf{n}).$$

Notice that the excess function refers to a real physical state whilst the residual functions depend on a hypothetical ideal gas reference state. The residual function must therefore take phase condensation into account, whereas the excess function tacitly can rely on direct observations of the condensed phase.

4.3.1. Gibbs and Helmholtz energy residuals

The canonical variables of Gibbs energy include temperature and pressure. This makes it possible to compare the chemical potentials of the components in a real fluid with those of the same components in the ideal gas state when the phases are both at the same *temperature, pressure* and *composition*. Using what we already know about G^{ig} allows us to define the residual Gibbs energy as:

$$\text{Eq. -4.14} \quad G^{\text{r,p}}(T, p, \mathbf{n}) \equiv G(T, p, \mathbf{n}) - G^{\text{ig}}(T, p, \mathbf{n}).$$

As $p \rightarrow 0$, all fluids approach virtually ideal properties in the sense of the pressure of the fluid approaching NRT/V when the volume increases to infinity. By taking the proper limits it is possible to rewrite Eq. -4.14 as

$$G^{\text{r,p}}(T, p, \mathbf{n}) = \int_0^p (V - V^{\text{ig}}) d\pi = \int_0^p \left(V(\pi) - \frac{NRT}{\pi} \right) d\pi.$$

Here, π stands for the integrated pressure whereas the system pressure p is in the upper limit of the integral. The functional form of the chemical potential $\mu_i = (\partial G / \partial N_i)_{T, p, N_{j \neq i}}$ is valid for all proper Gibbs energy functions, including $G^{\text{r,p}}$. This allows us to define the residual chemical potential as

$$\begin{aligned} \mu_i^{\text{r,p}}(T, p, \mathbf{n}) &\equiv \left(\frac{\partial G^{\text{r,p}}}{\partial N_i} \right)_{T, p, N_{j \neq i}} \\ &= \int_0^p \left[\left(\frac{\partial V}{\partial N_i} \right)_{T, \pi, N_{j \neq i}} - \frac{RT}{\pi} \right] d\pi \equiv \int_0^p \left(\bar{v}_i - \frac{RT}{\pi} \right) d\pi, \end{aligned}$$

where $\bar{v}_i \equiv (\partial V / \partial N_i)_{T, \pi, N_{j \neq i}}$ is defined as the *partial molar* volume of the component i . For historical reasons it is customary to rewrite the residual potential as

$$\text{Eq. -4.15} \quad RT \ln \varphi_i \equiv \mu_i^{\text{r,p}}(T, p, \mathbf{n}),$$

where $\varphi_i(T, p, \mathbf{n})$ is the *fugacity* coefficient of component i notwithstanding the rapid development of equations of state in the alternative form $p = p(T, V, \mathbf{n})$. Changing the free variable from p to V makes Helmholtz energy a better starting point than Gibbs energy. But φ_i measures the difference between a real fluid and its ideal gas approximation at a given pressure—not a given volume. This contradiction leads to a non-canonical description which shall not be pursued any further here. If, however, we redefine the residual Helmholtz energy as

$$A^{\text{r,v}}(T, V, \mathbf{n}) \equiv A(T, V, \mathbf{n}) - A^{\text{ig}}(T, V, \mathbf{n}),$$

the variables are again canonical, and we can use the same approach as for residual Gibbs energy at the beginning of this section. The alternative departure function can be written

$$A^{\text{r,v}} = \int_{\infty}^V \left(\frac{NRT}{v} - p(v) \right) dv,$$

which is perfectly well suited for building consistent thermodynamic frameworks.

4.3.2. Excess Gibbs Energy

Whereas the integration of a complete set of equations of state was successful in Section 4.2.4, it will not be helpful when we now start talking about solid phases. Solid phases cannot be formed from the gas phase in a continuous manner like a liquid can (not according to our present knowledge). For all solid phases, and many complex liquids, we must therefore rely on a different set of formulae. The most straightforward procedure is to jump-start from an Euler integrated form of Gibbs energy called the excess Gibbs energy $G^{\text{ex}} \equiv N g^{\text{ex}}$. This is an obvious choice because G^{ex} depends on mole numbers only, and not on volume and mole numbers in combination, as $A^{\text{r,v}}$ does.

Before we enter the discussion of excess Gibbs energy models we must first define what an ideal mixture looks like. There is no need for a physical model at this point—only a set of conditions that holds irrespective of which model we are going to use later. According to IUPAC, there is no mixing term for the enthalpy and volume of the ideal mixture. These two properties depend solely on the pure component values h_i^* and v_i^* . Recognizing H and V as partial derivatives of G/T yields the expressions:

$$\left(\frac{\partial(G^{\text{im}}/T)}{\partial(1/T)} \right)_{p, \mathbf{n}} = H^{\text{im}} = \sum_i N_i h_i^*(T, p) \equiv H^*,$$

$$T \left(\frac{\partial(G^{\text{im}}/T)}{\partial(p)} \right)_{1/T, \mathbf{n}} = V^{\text{im}} = \sum_i N_i v_i^*(T, p) \equiv V^*,$$

It follows that the properties of G^{im}/T must be quite similar to H^{im} and V^{im} , possibly with the exception of an unspecified non-linear term in \mathbf{n} that is not coupled to T or p . The same argument applies to G^{im} . From physical chemistry the non-linear term is known as the ideal entropy of mixing S^{im} . This completes the physical picture of the mixture model, but in order to elucidate better how

the many contributions depend on the composition of the mixture we shall look at the chemical potential μ_i rather than G itself. The Gibbs energy of the mixture is anyhow given as $G = \sum_i \mu_i N_i$:

$$\begin{aligned} \mu_i(T, p, \mathbf{n}) &= \mu_i^*(T, p_o) + \int_{p_o}^p v_i^*(T, \pi) d\pi \\ &\quad - T \bar{s}_i^{\text{im}}(\mathbf{n}) \\ &+ \mu_i^{\text{ex}}(T, \mathbf{n}) + \int_0^p [\bar{v}_i(T, \pi, \mathbf{n}) - v_i^*(T, \pi)] d\pi. \end{aligned}$$

In this equation $\mu_i^*(T, p_o)$ stands for the standard state chemical potential, v_i^* is the pure component molar volume, \bar{v}_i is the partial molar volume in the mixture, \bar{s}_i^{im} is the partial molar entropy in the ideal mixture and μ_i^{ex} is the excess chemical potential at zero pressure. The integral form, where each line in the previous equation is provided a separate symbol, is:

$$G(T, p, \mathbf{n}) = G^*(T, p, \mathbf{n}) + G^{\text{im}}(T, \mathbf{n}) + G^{\text{ex}}(T, p, \mathbf{n}).$$

The rest of the current section is devoted to excess Gibbs energy models at fixed temperature and pressure. Thermodynamically, it is sufficient to make sure G^{ex} is an Euler homogenous function of the first order, or, equivalently, that G^{ex} is homogeneous of order zero. However, G^{ex} must of course also be physically acceptable. In particular, and valid for all non-electrolytes, the activity coefficient of the substances must be finite at all concentrations. But, this statement is premature since we have not properly defined what exactly an activity coefficient is. We shall therefore rephrase the statement so that $g^{\text{ex}}/x_i x_j$ must be non-zero and finite in each pure component corner in the composition space. Hence, for each binary ij the following must be true:

$$\lim_{\substack{x_i \rightarrow 0 \\ x_j \rightarrow 1}} \frac{G^{\text{ex}}}{x_i x_j} = K_{ij}; \quad K_{ij} \in (0, \infty).$$

The simplest possible model is the regular mixture for which K_{ij} is constant over the entire composition range. For a binary system we get:

$$G^{\text{ex,reg}} = x_1 x_2 K_{12}.$$

A generalization leads to K_{12} as a function of the composition. The expressions of Margule and Redlich–Kister are of polynomial functions of this type:

$$G^{\text{ex,R-K}} = x_1 x_2 \sum_{n=0}^{0,1,2,\dots,N} K_{12}^{(n)} (x_1 - x_2)^n \simeq x_1 x_2 \mathcal{P}_N(x_1 - x_2).$$

By normalizing the fractions x_1 and x_2 in a different way, by saying

$$\phi_1 \equiv \frac{q_1 N_1}{\Phi} \quad \text{and} \quad \phi_2 \equiv \frac{q_2 N_2}{\Phi} \quad \text{where} \quad \Phi \equiv q_1 N_1 + q_2 N_2,$$

and making allowance for $g^{\text{ex}} \equiv G^{\text{ex}}/\Phi$, we get the Wohl expansion, which is also used in the non-configurational part of the Flory–Huggins model for monomer–polymer mixtures. All of these models are in a sense polynomial models. Some mixtures behave strongly as a non-polynomial, however, and a rational function of two polynomials of the orders N and $M > N$ might perform better. The

Van Laar and Hildebrand–Scatchard models are the simplest models of this type. On general terms we can write:

$$g^{\text{ex,VLaar}} = x_1 x_2 \mathcal{R}_{N,M}(x_1 - x_2).$$

Another line of thought leading to the so-called local composition models was developed in the 1960s. The models are based on the idea that the composition of a mixture is not entirely uniform throughout the bulk phase—not on a microscopic level. There is no hard theory to support this idea either, but it has an appealing physical basis for sure. Progress in this field lead to three well-known models. These are the Wilson model

$$g^{\text{ex,Wilson}} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1),$$

which actually is an extension of the Flory–Huggins model. Then there is the Non-Random-Two-Liquid model of Renon and Prausnitz

$$g^{\text{ex,NRTL}} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right),$$

and finally the UNiversal QUAsi-Chemical model (UNIQUAC) by Abrams and Prausnitz, which like the Flory–Huggins model consists of a combinatorial term and a residual term. At this point the expressions are becoming quite complex and we leave it for the interested reader to look them up yourself.

All the excess functions we have seen so far are written for binary systems. This is done on purpose in order to illustrate the basic principles of the modelling, but we can still define the activity coefficient based on the assumption that a multicomponent model is at our disposal:

$$\text{Eq. -4.16} \quad RT \ln \gamma_i \equiv \mu_i^{\text{ex}}(T, p, \mathbf{n}) = \left(\frac{\partial G^{\text{ex}}}{\partial N_i} \right)_{T, p, N_{j \neq i}}.$$

There is a close link between the fugacity coefficient in Eq. -4.15 and the activity coefficient in Eq. -4.16. The former is a measure for the deviation of the real state from an ideal gas at the same T, p, \mathbf{n} , whereas the latter uses the pure substance i at the same T, p as a reference. Hence, by calculating the fugacity coefficient of the pure substance as $\varphi_i^*(T, p)$ we get:

$$RT \ln \gamma_i \equiv \frac{\varphi_i(T, p, \mathbf{n})}{\varphi_i^*(T, p)},$$

but just like in the case of the fugacity coefficient there is no real need for the activity coefficient in the analysis of thermodynamics of mixtures. The prime function is, and will always be, the excess Gibbs energy. All mixture properties of interest can be derived from G^{ex} by differentiation.

4.4. The CALPHAD approach

‘CALPHAD’, short for “CALculation of PHase Diagrams”, is a form of thermodynamic modelling where the future state of a system is predicted based on the laws of thermodynamics. However, the foundations and scope of the approach have expanded since its inception, so CALPHAD is now synonymous with the computer coupling of phase diagrams and thermochemistry.

CALPHAD-based calculations provide data about which phases will be present (and at what concentrations) in a system that has reached a state of equilibrium under certain temperature and composition conditions. Calculation results are typically presented as diagrams that show which phases are present in a multicomponent system given varying conditions that are presented along the X- and Y-axes. However, the calculations can also result merely in information about a single equilibrium or in a diagram that plots a specific property of the system (the molar volume of a specific phase for example) under various conditions.

The theoretical basis of CALPHAD is thermodynamics. According to this theory, the so-called Gibbs energy of a system evolves, other things being equal, steadily toward its minimum value. At the minimum Gibbs energy value, the system will remain in a stable equilibrium state and will only change if it is perturbed from the outside in some way.

The calculations are based on databases that contain a set of parameters which describe thermodynamic functions of all phases of a system. The parameters are set by database developers who optimise the parameter values in light of a wide range of weighted experimental measurements as well as theoretical calculation results (ab initio data).

If the Gibbs energy is accurately described for all phases of a system as functions of composition, temperature and pressure, then these thermodynamic functions can be used to calculate all equilibria, phase diagrams, driving forces and thermodynamic properties (e.g. entropy, heat capacity or thermal expansivity). This means that they can be used to predict what will happen when the material is prepared or processed in various ways. The challenge for developers of CALPHAD models and databases is to find out what the correct Gibbs energy functions are.

Databases are primarily based on information from binary and ternary material systems, but by using relatively simple models of phases and data about the “lattice stabilities” of elements and their binary interactions, it is possible to extrapolate from a calculation to make predictions about higher-order systems. The utility of the CALPHAD-based calculations depends on there being reliable and comprehensive databases for the systems that one is interested in.

Note that the “CALPHAD approach” can refer to three different aspects of thermodynamic modelling: first, scientific research and model development for understanding, for example, binary and ternary systems. Second, database development and data optimisation with respect to certain concrete systems. And finally, the applied use of CALPHAD to make predictions about real materials and in various applied settings.

4.4.1. History

The history of CALPHAD goes back to the 1930s when Carl Hugo Johansson, a physicist at the Royal Institute of Technology (KTH) in Stockholm, published an assessment of part of an Fe-C system. This may have been the very first modern CALPHAD assessment. In part inspired by Johansson’s paper, the PhD student Larry Kaufman and his supervisor Professor Morris Cohen evaluated a model of the Fe-Ni system in the 1950s at MIT. In 1970, Kaufman and Harold Bernstein published a book with descriptions of the Gibbs energy expressions for many more phases of binary and ternary alloy systems. The book demonstrated the power and practical use of the CALPHAD methodology.

In 1968, Hillert published a paper which demonstrated the predictive power that could be achieved if experimental data about thermodynamic properties and phase diagrams were used with computer

programs. Before this, applying the CALPHAD methodology involved drawing phase diagrams with a ruler, based on Gibbs energy curves calculated by hand or with a desk calculator.

The use of computers to do calculations really got started in the 1970s. During this decade there was also significant development of solution models and calculations techniques. CALPHAD-based calculations could now, for example, take magnetic contributions into account. CALPHAD was also developed to make use of the results of theoretical ab initio calculations. This made it possible to generate data points for thermodynamic properties and phase diagrams for which experimental data were missing. In addition, computer software for fitting predictions of models to a variety of different types of data, by using the least squares method, were developed in the late 1970s and the 1980s.

In the 1970s, an international community of CALPHAD researchers and practitioners also emerged. The first and second CALPHAD meetings were held in 1973 and 1974 and the scientific journal CALPHAD was launched in 1977. In 1979, CALPHAD research groups in Europe founded the organisation Scientific Group Thermodata Europe (SGTE). Crucial for the development and adoption of CALPHAD was SGTE's publication of a free and open unary database for a large number of pure elements in 1991. Before this common database, different research groups often used different data for the elements. SGTE has also published two commercially available databases: a substance database, which contains data for inorganic compounds and gases, and a solutions database, which contains data on binary and ternary systems (as well as some systems of an even higher order). SGTE has been updating all of these databases continuously. A subset of the solutions database that only contain data about binary systems is also freely available from the organisation. In the 1980s and 1990s, the use of the CALPHAD methodology continued to spread in academia as well as industry. Several powerful software packages were released during this time (e.g. Thermo-Calc and FactSage). These were typically developed by research groups in academic settings, but in the 1990s and 2000s, the software packages became the basis for commercial companies that started to sell both software tools and thermodynamic databases.

Since its inception in the 1950s, the foundations and scope of the CALPHAD approach have expanded considerably. Coupled with information about the kinetic properties of different material systems, a temporal dimension can be added to simulations. Various kinds of diffusion phenomena can be simulated. Today, it is the most widely used methodology for solving practical material design problems in many industries.

In this current decade, CALPHAD has become part of efforts to revolutionise materials engineering associated with ICME and the Materials Genome Initiative (MGI), a major funding scheme that was announced in 2011 by US President Barack Obama.

Today, CALPHAD is an established tool in material science and materials engineering in academic as well as industrial settings.

4.4.2. Crystallography and models of phases

The CALPHAD method is distinguished from mere curve fitting by physically based model descriptions of the phases. These model descriptions are the foundation for reliable extrapolation of CALPHAD descriptions of binary and ternary systems to higher order systems and are crucial for coupling thermodynamic calculations with other simulations such as diffusion processes. For development of a good model description, the structural properties of the phase must be taken into account. In the

case of crystalline phases this means that the crystal structure of these phases should serve as a blueprint for modelling the composition dependence of the thermodynamic functions.

In a crystalline solid phase, the atoms are arranged in a regular, periodic pattern. The smallest unit to describe this structure is the unit cell. The relative arrangement of the atoms within this unit cell is the crystal structure. The symmetry of the unit cell is described by the space group, and the position of the atoms are described by the Wyckoff position. The space group symmetry determines the point symmetry of the Wyckoff position and its multiplicity, i.e. how many atoms are generated by the symmetry in the unit cell. Each space group has one general Wyckoff position where each of the coordinates can have any value between zero and less than unity. Depending on the space group, these can range from none to many special positions where the values of the coordinates are constrained. These constraints are determined by the symmetry of the space group such as a fixed value or that two or all three must have the same value or are offset by a fixed value. If all coordinate values are fixed, this Wyckoff position can only be occupied once in the crystal structure, otherwise there is no theoretical limit to how often a Wyckoff position with different coordinate values can be occupied.

The Compound Energy Formalism (CEF, also called sublattice model) is very well suited for the description of ordered phases but is also suited for the description of the gas phase, regular solutions and liquids with short range order. The basis of this formalism is that a phase consists of different sublattices that are occupied by a number of species which can be atoms, molecules, ions or vacancies. The two simplest cases within the CEF are a description consisting of only one sublattice, which describes the gas phase and regular solutions, and the description of a phase with only one species on each sublattice, which describes a stoichiometric compound.

The first step in selecting a model description is based on the crystal structure where initially one sublattice is assigned to each Wyckoff position and the site occupation is noted. The multiplicity of the site becomes the stoichiometric factor of this sublattice. Some phases, such as oxides or salts, can be highly ordered while some may show a lesser degree of ordering, such as the σ phase in the Cr-Fe system. The second step is to examine how these occupations change on deviation of stoichiometry, i.e. whether substitution occurs, vacancies are found or interstitials are formed. Ideally this is done for both the system being modelled as well as for other systems in which this phase occurs to ensure that the selected model will be compatible with higher order systems. This analysis provides an idea of which elements occur on each sublattice. The crystal structures of many phases in metallic systems are fairly simple and may have only three or fewer Wyckoff sites. However, for phases with complex crystal structures which have four or more Wyckoff sites, it may be useful to simplify the description by combining two or more of the Wyckoff sites into one sublattice (Table 4.2).

In the past, one driver for simplifications was to reduce the numbers of model parameters that need to be determined. The majority of these model parameters are those describing the end-member phases. End-member phases are formed when each sublattice is occupied by only one kind of species, i.e. atom, ion or vacancy, and one usually represents the phase with ideal stoichiometry while the remaining end-members are hypothetical and are assumed to be metastable. For an n -component phase where all elements occur on all k sublattices the number of end-members is n^k . Today Density Functional Theory (DFT) calculations allow one to obtain values for these hypothetical end-members. However, another reason for considering the simplification of a description is that,

with an increasing number of elements occurring in a specific phase, the calculation will become increasingly sensitive to the quality of the start values of the species composition on each of the sublattices.

In the early days of using the CEF, the crystal structure may have been used as a guide for the model description, but the model selection was finally governed by the convenience of simplicity that allowed it to cover the homogeneity range of the phase. This practice may work well for the description of binary and ternary systems but problems may be encountered when the descriptions of a large number of systems are combined into a database for multicomponent systems. These problems are usually model incompatibility between the descriptions of different systems or unrealistic extrapolation behaviour in a higher component system. Therefore, simplifications must be selected with great care and often criteria, such as preferred occupation, coordination number, coordination polyhedron and point symmetry, must be used. Instead of the combination of sublattices, the number of model parameters can also be reduced by introducing constraints between them. For example, experimental data may indicate ordering between two sublattices in a phase in specific systems while there is no such indication in other systems. This can be taken into account by the selection of appropriate constraints. Another way of introducing constraints is the definition of so-called "exchange energies". These exchange energies can be defined for one species substituting for another on a specific sublattice or for an ionic species being replaced by the same element but with a different charge on the same sublattice

Model selection should also reflect the relationship between different but related structures. The most common cases are order/disorder forms and the filling of vacant sites with interstitials. Important order/disorder phases that should be treated by special model descriptions are those that are based on the fcc, bcc and hcp structures. These phases are modelled with multiple sublattices to describe the ordered variants. The cases that are usually described are the $L1_2$ and $L1_0$ ordering of the fcc, the B2 and DO_3 ordering of the bcc and the DO_{19} ordering of the hcp. The model description usually consist of two parts, one describing the disordered phase and the other describing the contribution from ordering. Constraints for the model parameters of the ordering part are derived from the number of first and second, for bcc ordering, nearest neighbour pairs. This treatment ensures that the phases can undergo a second order phase transformation. The Cluster Site Approximation (CSA) is another formalism using sublattices that can be used for describing order/disorder phases based on the fcc and hcp structures. The CSA is based on the tetrahedron approximation used in the Cluster Variation Method in conjunction with a generalized quasi-chemical method.

The relationship between different crystal structures is also an important factor that needs to be considered for model selection. Different prototypes do not necessarily mean that the phase must be modelled as different phases, for example, if the prototypes are different but the space group and Wyckoff sequence are identical, as is the case for the DO_3 ($AlFe_3$) and the $L2_1$ ($AlCu_2Mn$, Heusler) structures. Both structures have the same space group $Fm\bar{3}m$ with the same Wyckoff sequence (a b c), which means that the two structures are not different at all. The only difference is that the DO_3 is a binary prototype while the $L2_1$ is a ternary prototype where the c and b positions in one case are occupied by the same elements and in the other case by different elements. Therefore, these two phases should be described as the same phase. Another case is where two crystal structures have the same space group but a continuous transition from one structure type to another structure type is possible. Many of these cases are the filling of interstitial sites. For example, many carbides and

nitrides have the same close packed structure as the pure metal with interstitial sites fully or partially filled. These phases should, therefore, be modelled as one phase. However, it may be useful to describe identical phases with independent descriptions if it is unlikely that they will form homogeneity ranges in a higher component system, such as a halide and a carbide, which both have the rocksalt structure.

4.4.3. Models of Composition Dependence

Ionic sublattice model

The ionic two-sublattice liquid (I2SL) model was developed to be used when there is a tendency for ionization in the liquid, which happens in liquid oxides and sulphides for example. The same model can be used both for metallic and oxide melts. At low levels of oxygen, the model becomes equivalent to a substitutional solution model between metallic atoms. Two sublattices are assumed, one containing charged cations and one containing charged anions, neutrals and vacancies. The

Table 4.2: Frequently used models for common solid phases

Phase	Model	Comment
Fcc_A1	$(A,B)_1(Va,C)_1$	Substitutional (A,B) solution with C interstitials
Bcc_A2	$(A,B)_1(Va,C)_3$	Substitutional (A,B) solution with C interstitials
Hcp_A3	$(A,B)_1(Va,C)_{0.5}$	Substitutional (A,B) solution with C interstitials
Fcc_L10, Fcc_L12	$(A,B)_{0.25}(A,B)_{0.25}(A,B)_{0.25}(A,B)_{0.25}(Va,C)_1$	4 sublattice, order/disorder formalism*
Bcc_B2, Bcc_D03	$(A,B)_{0.25}(A,B)_{0.25}(A,B)_{0.25}(A,B)_{0.25}(Va,C)_3$ $(A,B,Va)_{0.25}(A,B,Va)_{0.25}(A,B,Va)_{0.25}(A,B,Va)_{0.25}(Va,C)_3$	4 sublattice, order/disorder formalism*, (A,B,Va) includes structural vacancies
Hcp_D019	$(A,B)_{0.75}(A,B)_{0.25}(Va,C)_{0.5}$	2 sublattice, order/disorder formalism
C14_Laves	$(A,B)_1(A,B)_{1.5}(A,B)_{0.5}$	3 sublattices, constraint may be employed if there is no ordering between the second and third sublattice
C15_Laves	$(A,B)_1(A,B)_2$	
Sigma	$(A,B)_{10}(A,B)_{16}(A,B)_4$	Also simplified to $(A,B)_1(A,B)_2$, $(A,B)_{10}(A,B)_{16}(A,B)_4$
Mu	$(A,B)_1(A,B)_2(A)_4(A,B)_6$	
Chi	$(A,B)_5(A,B)_{12}(A,B)_{12}$	Also simplified to $(A)_5(A,B)_{12}(A,B)_{12}$

* If only L1₂ or B2 ordering is described a 2 sublattice, order/disorder formalism can be used.

complication for an ionic liquid is that the number of sites on the cation sublattice and anion sublattice vary with the composition to preserve electroneutrality.

In I2SL, the number of sites on each sublattice is a function of composition in order to maintain electroneutrality. The sublattice description can be written as

$$\left(C_i^{v_i^+} \right)_P \left(A_j^{v_j^-}, Va, B_k^0 \right)_Q$$

where $C_i^{v_i^+}$ are cations, $A_j^{v_j^-}$ are anions with charges v_i^+ and v_j^- , respectively, and B_k^0 are neutral species. It is assumed that the vacancies Va have an induced negative charge with a valency equal to the average valency on the cation sublattice. The number of sites on each sublattice, P and Q , are given by the average charge on the other sublattice, i.e.

$$Q = \sum_i v_i^+ y_{C_i}$$

$$P = \sum_j v_j^- y_{A_j} + \left(\sum_i v_i^+ y_{C_i} \right) y_{Va} = \sum_j v_j^- y_{A_j} + Q y_{Va}$$

In the syntax of a commonly used thermodynamic database format the phase-type code Y is attached to a phase name after a colon, e.g. LIQUID:Y, means that the phase is of this type.

Associate model

The associate model can be treated within the default framework. Use of the model implies that additional constituents are added such that a phase obtain additional internal degrees of freedom. This may be needed for describing experimental data for the liquid phase for example. The existence of molecules as constituents sometimes needs to be postulated, but the life-time of such a molecule may be so short that it cannot be found as an independent entity. The notion of *associate* has therefore been introduced to capture tendencies for ordering around certain compositions. The existence of associates is supported if there is a tendency for covalent bonding between the elements.

Modified quasichemical model

This model is similar to the associate model, but different with respect to the configurational entropy contribution.

4.4.4. Model of nano-size effect

As the size of a nano-scale system decreases, the surface effect increases in significance. This means that the contribution of surface Gibbs energy must be considered when calculations are done on nano-scale systems. The surface Gibbs energy of a nano-scale system is described as a function of the particle size.

Accordingly, the total Gibbs energy of an alloy system is composed of the bulk and surface terms.

$$G^{Total} = G^{Bulk} + G^{Surf}$$

For a nanoparticle (NP) with radius r , the surface Gibbs energy is given by

$$G^{Surf(NP)} = \frac{2\sigma V}{r}$$

For a nanowire (NW) with radius r and length l ($r \ll l$), the surface Gibbs energy is expressed by

$$G^{Surf(NW)} = \frac{\sigma V}{r}$$

It is likely that the surface Gibbs energy of a nanofilm (NF) with thickness t is

$$G^{Surf(NF)} = \frac{(\sigma + \sigma^I)V}{t}$$

where σ is the surface tension, σ^I is the interface tension (including interface stress) and V is the molar volume. The surface tension of liquid and solid alloy can be computed using Butler's equation with known surface tension and density of pure metals as well as the bulk excess Gibbs energy from the scientific literature.

The expression of the Gibbs energy of a nano-scale system is not so different from that of bulk system. For example, the Gibbs energy of an alloy nanoparticle can be described by

$$G^{Total(NP)} = \sum X_i G_i^{o(NP)} + RT \sum X_i \ln X_i + G^{EX(NP)}$$

For simplicity, we may assume that the excess Gibbs energy has a Redlich-Kister type composition dependence:

$$G^{EX(NP)} = \sum_i \sum_{<j} X_i X_j \sum_{v=0}^m L_{ij}^{(v)} (X_i - X_j)^v + \sum_i \sum_{<j} \sum_{<k} X_i X_j X_k L_{ijk} + \dots$$

Here, the parameter $L_{ij}^{(v)}$ is expressed by

$$L_{ij}^{(v)} = f_1 \left(\frac{1}{r} \right) + f_2 \left(\frac{1}{r} \right) T + f_3 \left(\frac{1}{r} \right) T \ln T + \dots$$

The function f_m ($m = 1, 2, 3, \dots$) is simply given as a linear function of inverse of the particle's radius.

$$f_m = a_m + \frac{b_m}{r}$$

Therefore, when the particle radius becomes infinite, the excess Gibbs energy becomes the same as the Gibbs energy of the bulk system.

The thermodynamic parameters of an alloy nanoparticle system can be re-optimised by following this procedure:

- (1) Collect measurements of thermo-physical properties such as surface tension and molar volume of pure liquids and solids as well as a thermodynamic dataset about the bulk system.
- (2) Determine the surface tension of pure solid phase from the melting behaviour of nanoparticles. (Note that a correction factor for the surface tension of pure solid due to surface orientation and edge/corner effect is needed.)
- (3) Determine the molar volume of the various pure solid phases and intermetallic compounds including hypothetical ones.
- (4) Calculate the surface tension of liquid and solid alloys using Butler's equation.
- (5) Determine the standard Gibbs energy of pure elements as a function of the particle size.
- (6) Optimise the excess Gibbs energy as a function of the particle size.

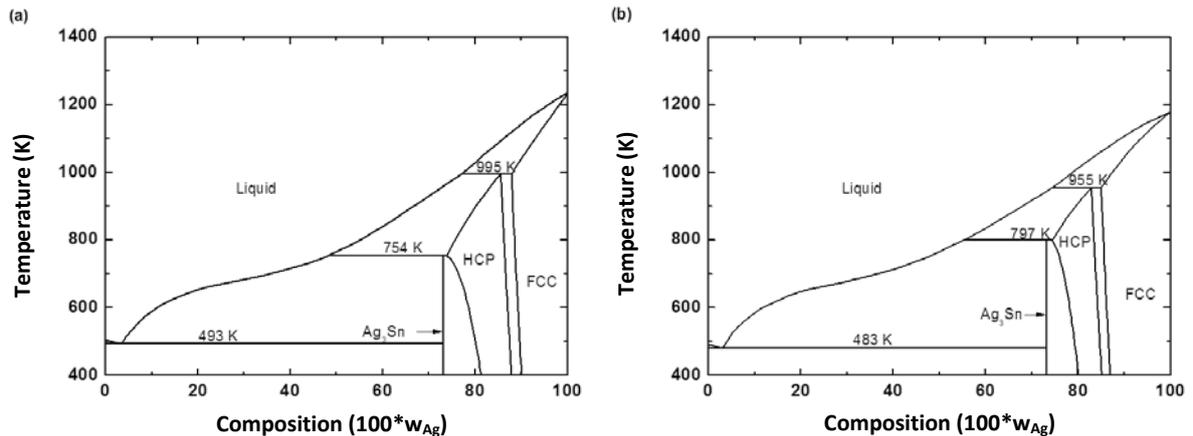


Figure 4.1: The calculated phase diagram of Ag-Sn alloy: (a) bulk and (b) nanoparticle with $r = 20$ nm. Reprinted from [ref14] with kind permission of Elsevier.

Figure 4.1 compares the calculated bulk and nano phase diagrams of Ag-Sn alloy. The validity of the calculated phase diagrams may be confirmed by experimental data. In-situ TEM or DSC analyses are frequently used to determine the phase transformation of a small-scale system. For more details on modelling and experiments, the reader is referred to the references in Section 4.9.

4.4.5. CALPHAD databases

The utility of CALPHAD-based simulation tools depends on reliable databases being available for the kinds of material systems being investigated. A database is typically focused on a certain class of alloys or other materials. It is important to realise that a CALPHAD database is not a collection of tagged and interlinked data. Rather, it contains the parameter values of the Gibbs energy functions defined by the thermodynamic models of the phases that are included in the database. It can also contain additional information, such as the sources of different parameters, instructions for its use, limitations and so on. The database is stored in a plain text file format, although commercial databases are almost always encrypted before they are sent to the customer. The file size is relatively small; even a large multicomponent database rarely consists of more than one or two megabytes of data.

CALPHAD databases are available for a broad range of applications, including steels and Fe alloys, Al, Mg, Ni and Ti alloys, cemented carbides, solders, noble alloys, nuclear applications, salts, oxide ceramics, slags and aqueous solutions. However, there are still large uncharted areas for new materials and less extensively investigated materials. This even includes particular combinations of alloying elements in otherwise well-known alloy systems. If one considers that 80 elements could be of some practical use, then there are about 3000 possible binary systems and 80,000 possible ternary systems. Of the binary systems a large fraction have at least been tentatively investigated experimentally and a reasonable fraction have been extensively investigated and/or thermodynamically modelled. Of the ternary systems only a small fraction have been modelled thermodynamically and for a large fraction there is no knowledge at all.

Most databases have a particular application or group of applications in mind, such as steels. The database must then include all binary systems and several ternary systems involving Fe. The database should also contain all other binary systems, with the exception of impurity elements (such as S, P or O in steel) where the most important binary systems would be sufficient. The database should also contain further important ternary and higher order systems. The fraction of ternary

systems included in the database can be used as a measure of the (potential) quality of the database. The database might not include all phases from the included datasets, but only the phases that are relevant for the application in mind. This can be helpful because the user is not confronted with a large number of irrelevant phases, but has the consequence that many phase diagrams from the included datasets will not be correctly reproduced. Also, it may not always be obvious which phases are relevant.

A CALPHAD database is “constructed” from datasets for the unary (elemental), most binary, important ternary and a few higher order systems. Most of the binary and ternary datasets are taken from the open literature where they are published as thermodynamic assessments (or evaluations). In a large database, datasets are compiled from a larger number of different sources. Creating a high-quality database is not just a matter of collecting these individual datasets, but requires adjustments and reoptimisation of some of the datasets, unification of incompatible models, identification of missing parameters and extensive checking. These issues are discussed in more detail in Section 4.4.6. The level of quality and scope of individual datasets can be very different. The quality of a database is strongly dependent on the quality of the datasets included, the fraction of ternary and higher order systems and on the care with which it has been constructed.

Since the Gibbs energy functions for the elements are used in several different datasets coming from different sources it is of utmost importance that everyone uses the same Gibbs energy functions. Otherwise it would not be possible to combine different datasets in databases. Today the SGTE unary database, originally published by Dinsdale [ref2] and regularly updated, is used almost universally as a source for the element datasets.

Although the pressure is a thermodynamic state variable, the Gibbs energy models used in CALPHAD databases usually do not include a pressure dependence except for the gas phase, which is modelled as an ideal gas. The ideal gas model is reasonable for ambient pressure (or lower), but ceases to be so at very moderate pressure. A few CALPHAD databases include molar volumes for the condensed phases. These molar volumes are modelled as temperature dependent, but not pressure dependent, and can be used to calculate the pressure dependence of phase equilibria between condensed phases at moderate pressure. Full pressure dependence requires the use of pressure dependent molar volumes, i.e. the use of an equation of state. This poses a number of modelling issues and, not least, a problem of a lack of experimental data. Full pressure modelling is, thus, very expensive and there is not much interest in the area of materials development and processing. So far, thermodynamic databases with full pressure modelling have only been developed in the geological community.

4.4.6. Database development and parameter optimisation

This section describes how datasets are derived and some of the issues encountered when they are used to develop a database. The description (i.e. the Gibbs energy functions with their determined parameter values) of a lower order system (binary, ternary, or, rarely, quaternary) that has been individually modelled is called a dataset. The process of deriving the Gibbs energy models and determining the parameter values is usually called a thermodynamic assessment or evaluation. This includes a critical review of all available experimental data and ab initio data relevant for the system, coding the data in a form that can be used by an optimisation program, performing the optimisation (or otherwise determine the parameter values) and documenting the results, typically in the form of a publication.

There are a few very specific circumstances that render the CALPHAD method its usefulness and it is important to be aware of those when modelling a system or building a database.

- The phase diagram is very sensitive to the relative Gibbs energies of the phases present, but not sensitive to the absolute values of the Gibbs energy (or rather the enthalpy and entropy). Therefore, a key point in the CALPHAD method is to model both phase diagram data and thermodynamic data at the same time. If one type of data is missing or inaccurate, the derived parameter values will not be reliable.
- Alloy thermodynamics is dominated by lattice stabilities and pair interactions. Therefore, (thermodynamic) extrapolation from binary to ternary and higher order systems for the included solution phases will be reasonable, provided that the binary parameters are reasonable. As a further result, there are rather few phases that are truly quaternary or higher order. A carefully constructed CALPHAD database will give reasonable results for e.g. a ten-component system that has never been investigated experimentally.
- The Gibbs energy for each phase is available for the complete concentration range for which its Gibbs energy model is defined, irrespective of whether the phase is stable for a specific composition. This means that the Gibbs energy can be calculated for any conceivable metastable (or even unstable) state. This is needed for the simulation of phase transformations.

The process of performing an assessment is described in some detail by Lukas et al. [ref10] and Schmid-Fetzer et al. [ref21]. Whereas, Lukas et al. [ref10] give a broad introduction to the basic machinery, Schmid-Fetzer et al. [ref21] concentrate on the many pitfalls that can be encountered. The latter also present a procedure to check datasets with respect to correctness, reasonability, accuracy and safety.

Starting with the modelling of a binary system the first step is to collect as much relevant information about the system as possible. This will mostly be publications from scientific journals, but will usually also include conference papers, reports, theses and further so called “grey” sources. Once sufficient information has been collected one has to decide which phases to include and which models to use. Terminal solution phases will usually be one (or more) of fcc, bcc and hcp (in addition to the liquid). These phases are always modelled as solid solutions and should, therefore, include both elements. For many common intermetallic phases, such as Laves, σ and μ , models have been defined, but there is not always agreement on which of the suggested models should be used. There is a tendency to use more complex models with several sublattices to better reflect the crystal structure of the phase. Such models generate a large number of model compounds whose Gibbs energies cannot be determined from experiment, but have to be estimated, or, better, calculated by ab initio methods. For ordered phases based on fcc, bcc and hcp, order-disorder models have been defined. These models require particular care in their handling. Intermetallic phases with a narrow and uncertain composition range should be modelled as stoichiometric compounds. Then, the experimental data points must be coded in such a way that they can be used for the parameter optimisation. This means that it should be possible to calculate the corresponding equilibrium using the current set of parameter values. The difference between the calculated and measured value divided by an uncertainty is the error that will be used in a least square minimisation. The parameter values are varied using a minimisation algorithm until a minimum is found. This is what is called parameter optimisation.

Very often it will be found that data are in conflict. This means that one or the other sets of data can be correct, but not both and also not the mean. It is therefore important to discard one of them from the optimisation, but it can be difficult to determine which one should be discarded. In the end a dataset has been derived which reproduces the phase diagram and thermodynamic properties with sufficient accuracy and provides reliable extrapolations. The dataset and the modelling process then need to be carefully documented, ideally in such a way that someone else could improve the dataset when new data or better models become available.

In ternary systems, in contrast to many binary systems, there are rarely sufficient data available to optimise all relevant model parameters. Usually, only a partial optimisation is possible and some parameters have to be estimated and fixed beforehand. The general procedure for modelling a ternary system starts with the three binary datasets. These are combined and an extrapolation of the solution phases, typically liquid, fcc, bcc and/or hcp, is made. This will often give an indication of whether the binary interactions are reasonable. Missing binary interactions need to be identified and given reasonable values or included in the ternary optimisation. For example the Cr–Mo system does not contain an fcc phase, but the Cr–Mo–Ni system does. If a binary fcc interaction in the Cr–Mo system is not determined the Cr–Mo–Ni system can still be modelled (by including a ternary fcc interaction), but extrapolations to higher order systems will not be good. An early version of the Thermo-Calc steel database could not accurately reproduce fcc-bcc equilibria for duplex stainless steels, which contain Cr, Mo and Ni, until the missing fcc interaction in the Cr–Mo system had been identified. When binary intermetallic phases dissolve the third element, this information has to be added to the model of the intermetallic phase. This generates further model compounds whose Gibbs energies must be determined. As a last step any ternary phases should be added. If a ternary phase is modelled with a solution model it will most probably generate binary model compounds. It is then important to make sure that they do not become stable in a binary system. A calculated ternary phase diagram is also a very good guide for further experimental work.

The general procedure to construct a CALPHAD database is not so different from modelling a ternary system. Several of the steps are in common; such as adding missing binary interactions, unifying compounds that belong to a single phase into a single model and determining Gibbs energies for model compounds not previously included. In contrast to binary and ternary datasets which are determined once and often not changed further, a database is usually extended and improved over a longer period of time.

All databases need to be checked extensively. There are two types of checking to be done. The first type is to recalculate all included lower order systems (datasets) in order to ensure the integrity and formal correctness of the database. This is needed to catch any misprints and phases that might appear in systems where they do not belong. The second kind of testing is to verify the database against a set of selected alloys. This can also be used for improvement of the database. Any discrepancies found need to be traced back to the relevant low order (binary or ternary) systems. These systems should then be modified or remodelled accordingly. However, it can be very difficult to identify the low order systems actually causing a mismatch for a complex alloy, see the previous example of the Cr–Mo system and duplex stainless steels. When changing a low order system it is necessary to at least check all higher order systems where this system is included. If e.g. Fe–Cr is changed, then all ternary systems with Fe and Cr will have to be checked and possibly modified. When a change is made to an element, this will influence a large number of systems in the database.

Thus, developing a multicomponent CALPHAD database requires considerable care and extensive checking.

4.4.7. Phase names

Finding an appropriate schema for naming is important for associating data with the phases they are describing and for retrieving experimental and computational data from conventional databases. Finding an appropriate naming schema is challenging because a phase name can serve as an identifier in both types of databases, conventional and CALPHAD-type. Inside a thermodynamic database the entries are tied together by the names of the phases. Although an abstract identifier would serve for this purpose, the phase name is also important information for the user. One could follow the example of the International Chemical Identifier (InChI) by constructing a string describing the various aspects that are needed to unambiguously describe a phase. However, the InChI can be lengthy and includes more information than needed, for example, in CALPHAD databases. For the user it is important that the phase name is brief and unique and that the phase it describes can easily be identified.

In the early days of alloy phase diagrams, phases were named using Greek letters. In unary systems letters were assigned from lower temperatures to higher temperatures, and in binary systems from the left to the right hand side of the system. This cannot work for a database that has even 10 elements since it will contain the descriptions of 45 binary systems and all their phases. This is easily illustrated by looking at the use of the letter γ . It describes the austenitic phase in Fe-alloys, the Ni-phase in superalloys, as well as the TiAl phase in Ti-Al based alloys, the $Mg_{17}Al_{12}$ phase in light weight alloys and the Cu_5Zn_8 phase in brass. On the other hand, the use of specific Greek letters has made those letters commonly recognized names for some of the topologically close packed phases, such as σ , μ or χ phases, that have large homogeneity ranges and rarely occur at ideal stoichiometries. The use of chemical formulae is also not practical because the same phase may occur in a number of the constituent binary subsystems of a multicomponent system, e.g. Laves phases with the ideal stoichiometry AB_2 occur in many of the binary systems that are relevant for superalloys. It is obvious that the use of a generalised chemical formula such as AB_2 is not feasible as there can be many different phases with the same ideal stoichiometry.

It would be convenient if a phase could be identified by a short name that is independent of the system. The identification of the crystal structure of phase could serve as a phase name, but the use of space group and Wyckoff sequence are not very intuitive. An early crystallographic data collection, Strukturbericht, devised a symbol system for crystal structures. This system uses letters for classes of compounds and numbers, with and without subscripts, to distinguish the different structures within the classes, for example, A for the elements, B for AB compounds, etc. It turned out that this system was not sustainable given the wide variety of different crystal structures, thus it was abandoned. However, the symbols for the simpler structures, such as A1 for fcc or A2 for bcc, are still popular and are used in many CALPHAD databases as phase names.

The IUPAC Redbook on Nomenclature of Inorganic Chemistry does not consider the use of Greek letters or the Strukturbericht designation as acceptable since they do not convey the necessary information and are not self-explanatory and recommends the use of the Pearson symbol for identification of the structure of a phase. However, the Pearson symbol is not unique, e.g. the symbol $cF8$ belongs to a number of different crystal structures. Although a crystal structure can be uniquely identified by its space group and its Wyckoff sequence, it gives no further information on

the character of a phase, for example, whether the phase belongs to the salt or carbide branch of a particular structure. In geo sciences it is customary to use the mineral name for phase identification. In a certain way one can view the CALPHAD practice of developing phase names using a mixture of Greek letters, Strukturbericht symbols, mineral names and stoichiometric formulae as a hybrid approach to provide phase names that are useful for the database developer and the user by being sufficiently intuitive to make it clear which phase is describe by the name.

It has become practice to use the term “fcc_A1” to describe disordered fcc solid solutions and the term “fcc_L12” for an ordered variant of this structure. A problem arises if these two phases are described as one phase that can be ordered or disordered, as this may result in the easy distinction of the two phases being lost to the user. In this case it is useful if the software determines the variant of the phase for the user. The same applies to compounds that are based on interstitial solutions in the phases of the pure elements, such as cubic and hexagonal nitrides. It should be noted that both structures must have the same space group to allow this continuous transition. For example, in the case of the fcc_A1 structure the filling of the interstitial octahedral site results in a continuous transition to a B1_carbide structure. Here again the software should determine which variant of the phase is encountered. It may be cumbersome to introduce all these provisions for the variants of a phase, but it enables the user to quickly recognize a phase without having to analyse the composition details of a phase. Table 4.3 presents suggestions for phase names and name variations for distinguishing different phase variants.

Table 4.3: Suggestions for names of common crystalline phases in CALPHAD type databases

Phase name	Strukturbericht designation	Prototype	Chemical formulae	Comment
Fcc_A1	A1	Cu	Al, Ni, Cu, ...	
Bcc_A2	A2	W	V, Cr, Mo, ...	
Hcp_A3	A3	Mg	Be, Mg, Ti, ...	
Fcc_B1	B1	NaCl	TiC, NbC, TaC, ...	
B1_Oxide	B1	NaCl	CaO, FeO, TiO...	
Bcc_B2	B2	CsCl	AlNi, AlFe, FeTi, ...	Ordered bcc
B2_Halide	B2	CsCl	CsCl, TlBr, KI	“Independent” B2
FCC_L10	L1 ₀	AuCu	AlTi, MnNi, FePt, ...	Ordered fcc
HCP_D019	D0 ₁₉	Ni ₃ Sn	AlTi ₃ , Co ₃ W, CoZr ₃ , ...	Ordered hcp
C14_Laves	C14	MgZn ₂	Cr ₂ Ti, HfMn ₂ , Ni ₂ U, ...	
C15_Laves	C15	MgCu ₂	Cr ₂ Ti, Co ₂ Ti, Ni ₂ Y, ...	
Mu	D8 ₅	Fe ₇ W ₆	Co ₇ Mo ₆ , Fe ₇ Nb ₆ , Ni ₇ Ta ₆ , ...	
Sigma	D8 _b	CrFe	AlNb ₂ , Cr ₃ Mn, Cr ₂ Re ₃ , ...	
Me3Si	...	PTi3	AsNb ₃ , GeZr ₃ , SiTi ₃ , ...	Limited to combination of transition metal with metalloid
Al3Fe	...	Al3Fe	Al3Fe, Al13Ru4	Only two compounds known with this structure
Al2Fe	...	Al2Fe	Al2Fe	No other chemistry known
Al3Co	Al3Co	Structure unknown

A short, easily recognisable phase name may be user friendly, but it has little value for linking the

phase to contents of non-CALPHAD databases. The challenge is that one phase in a CALPHAD database will likely be represented as a number of different phases in other databases. One solution to this problem would be to add identifier records for the phases that are described by this single description. This record could be constructed using the concept of the InChI and could contain records for formula, a general tag for the aggregate state, SOL, LIQ or GAS and tags with prototype (PT), Pearson symbol (PS), Strukturbericht designation (SD), space group (SG, using the number), Wyckoff sequence (WS) and site occupation (SO) of the Wyckoff positions and could look like one of the following examples:

Fe/SOL/PT:Cu/PS:cF4/SD:A1/SG:225/WS:a/SO:a:Fe describes pure fcc Fe;

Fe_{0.0897}/SOL /PT:Fe_x /PS:cF4/SD:A1/SG:225/WS:ab/SO:a:Fe:b:N describes the interstitial solution of N in fcc Fe;

TiC_{0.957}/SOL/PT:NaCl/PS:cF8/SD:B1/SG:225/WS:ab/SO:a:Ti:b:C describes off-stoichiometric compound TiC, note that site b, in contrast to the previous examples, is almost filled;

NiAs/SOL/PT:NiAs/PS:hP4/SD:B81/SG:194/WS:ac/SO:a:Ni:c:As describes the prototype NiAs;

Ni₂In/SOL/PT:Ni₂In/PS:hP6/SD:B82/SG:194/WS:acd/SO:a:Ni:c:In:d:Ni describes the prototype Ni₂In, note that the difference to the NiAs structure is that an additional site (d) is filled;

Au_{0.62}Pd_{0.74}Sn/SOL/PT:NiAs/PS:hP4/SD:B81/SG:194/WS:acd/SO:a:Au,Pd:c:Sn:d:Pd describes a phase with NiAs/Ni₂In structure where the d site is partially filled.

For identifying the liquid, instead of describing the crystal structure, one would identify the type of liquid (LT) and whether special species (SP) are identified:

AgAu/LIQ/LT:regular/SP:Ag,Au;

MnO/LIQ/LT:ionic/SP:Mn⁺²,Mn⁺³:O⁻²,Va-q.

The description of the gas phase would be a simple list of the species occurring in it:

As:/GAS/SP:As,As₂,As₄.

It should be noted that these suggestions currently do not cover amorphous or quasi-crystalline phases.

4.4.8. Reference states

When interpreting the values of some thermodynamic variables it is important to know which reference states the variable values are expressed relative to. These properties include Gibbs and Helmholtz energy values as well as chemical potentials, and activities are always expressed relative to some reference state. If reference states have not been properly defined for the values of these conditions they will be meaningless.

In substance or alloy solution CALPHAD databases, the data for each phase are described by Gibbs energies relative to the "Standard Element Reference" (SER), i.e. enthalpies that the pure elements have in their most stable phase at a temperature 298.15 K and a pressure of 100 kPa (1 bar).

The Gibbs energy of the SER state is referred to as G-HSER and is equal to H₂₉₈. Note that while the Gibbs energy of a phase has both enthalpy and entropy contributions, the entropy of a phase in the SER state is set to the entropy at 0 K and, according to the third law of thermodynamics, is zero.

Using G-HSER as a reference state is convenient since all data in a database can be expressed and relative to G-HSER so that data can be combined in thermodynamic calculations. All thermodynamic functions can be calculated directly from one or more derivatives of the Gibbs energy expression.

4.4.9. Database formats

A thermodynamic database, which stores the Gibbs energy function of every phase of interest in the system, is an essential part of CALPHAD-based thermodynamic calculations. The most widely used thermodynamic database format is the TDB format, which will be described here in some detail.

There are also other well-defined database formats. For instance, the Lukas program uses the DB format for phase diagram calculations. Details on this database format can be found in the book “Computational Thermodynamics: The Calphad method” [ref10]. FactSage has developed Compound databases and Solution databases on oxides, salts and other systems. The FactSage database format is described in [ref7][ref8].

A TDB database file is a plain text file that typically consists of four sections: **Elements**, **Functions**, **Type_Definitions** and **Phases**. Figure 4.2 illustrates the structure of a typical TDB file, this one describing the Al-Ni binary system with the key words highlighted in blue. Figure 4.2 is included for the purpose of illustration and is not a full database.

At the beginning of the file, the **Elements** section defines every component included in the database. Next to each element, the following information is listed: the stable structure at 298 K (for Al in the Figure 1, this is FCC_A1), the atomic weight (26.982 g/mol), the enthalpy (4577.3 J/mol) and the entropy (28.322 J/mol·K) of the element in its most stable state at at 298K.

In the **Function** section, the Gibbs energies of each pure element in each of its crystal structures are listed. The Gibbs energy of an element with a certain crystal structure is typically represented as a segmental function of temperature. The lower and upper temperature limits of each segment are specified at the start and end of each function segment. The “Y” after the upper segment limit indicates that there is another temperature segment above this upper limit. An “N !” indicates the end of the segmental function specification. These Gibbs energies are specified relative to the element’s SER state (see section 4.4.8). In the Function section, database developers can also define functions that can be used directly in the **Phase** section.

The **Type_Definition** section defines other features related to a particular phase. Simple characters are used to identify which **Type_Definitions** are used by a particular phase description. In Figure 4.2, “&” is used to define the magnetic parameters of the BCC_A2 phase and “N” specifies that L12_FCC has a disordered Gibbs energy contribution.

The major body of a TDB file consists of the **Phase** section. In this section, thermodynamic models are defined and model parameters are listed for each phase in the system. Some details are given below for the phases listed in Figure 4.2.

```

Element AL      FCC_A1      26.982  4577.3  28.322 ↓
Element NI      FCC_A1      58.69   4787    29.796 ↓
Element VA      VACUUM      0       0       0 ↓

Function GHSERAL 298.15 -7976.15+137.093*T-24.3672*T*ln(T)-0.00188466*T**2-8.77664e-007*T**3+74092*T**(-1); 700 Y
-11276.2+223.048*T-38.5844*T*ln(T)+0.018532*T**2-5.76423e-006*T**3+74092*T**(-1); 933.6 Y
-11278.4+188.684*T-31.7482*T*ln(T)-1.231e+028*T**(-9); 6000 N !

Function GLIQAL  298.15 11005-11.8419*T+7.934e-020*T**7+GHSERAL; 933.6 Y
10482.4-11.254*T+1.231e+028*T**(-9)+GHSERAL; 6000 N !

Function GBCCAL  298.15 10083-4.813*T+GHSERAL; 6000 N !

Function GHSERNI 298.15 -5179.16+117.854*T-22.096*T*ln(T)-0.0048407*T**2; 1728 Y
-27840.7+279.135*T-43.1*T*ln(T)+1.12754e+031*T**(-9); 6000 N !

Function GLIQNI  298.15 16414.7-9.397*T-3.82318e-021*T**7+GHSERNI; 1728 Y
18290.9-10.537*T-1.12754e+031*T**(-9)+GHSERNI; 6000 N !

Function GBCCNI  298.15 8715.08-3.556*T+GHSERNI; 6000 N !
Function U1ALNI 298.15 -14556.4+2.945*T; 6000 N !

Type_Definition & GES_A_P_D BCC_A2 Magnetic -1 0.4!
Type_Definition N GES_A_P_D L12_FCC dis_part DISORDER...!
Type_Definition ( GES_A_P_D FCC_A1 Magnetic -3 0.28!

Phase LIQUID % 1 1 ↓
Constituent LIQUID:AL:NI:↓
Parameter G(LIQUID,AL;0) 298.15 GLIQAL; 6000 N !
Parameter G(LIQUID,NI;0) 298.15 GLIQNI; 6000 N !
Parameter G(LIQUID,AL,NI;0) 298.15 -197088+30.353*T; 6000 N !
Parameter G(LIQUID,AL,NI;1) 298.15 5450; 6000 N !
Parameter G(LIQUID,AL,NI;2) 298.15 54624-11.383*T; 6000 N !

Phase AL3NI1 % 2 0.75 0.25 ↓
Constituent AL3NI1:AL:NI:↓
Parameter G(AL3NI1,AL;0) 298.15 -40463+5.312*T+0.75*GHSERAL+0.25*GHSERNI; 6000 N !

Phase AL3NI2 % 3 3 2 1 ↓
Constituent AL3NI2:AL:AL:NI:NI:VA:↓
Parameter G(AL3NI2,AL:AL:NI;0) 298.15 -41219+2.792*T+5*GBCCAL+GBCCNI; 6000 N !
Parameter G(AL3NI2,AL:NI:NI;0) 298.15 -428055+71.808*T+3*GBCCAL+3*GBCCNI; 6000 N !
Parameter G(AL3NI2,AL:AL:VA;0) 298.15 30000-3*T+5*GBCCAL; 6000 N !
Parameter G(AL3NI2,AL:NI:VA;0) 298.15 -356836+66.079*T+3*GBCCAL+2*GBCCNI; 6000 N !
Parameter G(AL3NI2,AL:AL,NI;0) 298.15 -38157; 6000 N !
Parameter G(AL3NI2,AL:AL,NI,VA;0) 298.15 -23319; 6000 N !

Phase DISORDER % 1 1 ↓
Constituent DISORDER:AL:NI:↓
Parameter G(DISORDER,AL;0) 298.15 +GHSERAL; 6000 N !
Parameter G(DISORDER,NI;0) 298.15 +GHSERNI; 6000 N !
Parameter G(DISORDER,AL,NI;0) 298.15 -16367+12*U1ALNI; 6000 N !

Phase L12_FCC % N 2 0.75 0.25 ↓
Constituent L12_FCC:AL:NI:AL:NI:↓
Parameter G(L12_FCC,AL:AL;0) 298.15 0; 6000 N !
Parameter G(L12_FCC,NI:AL;0) 298.15 3*U1ALNI; 6000 N !
Parameter G(L12_FCC,AL:NI;0) 298.15 3*U1ALNI; 6000 N !
Parameter G(L12_FCC,NI:NI;0) 298.15 0; 6000 N !
Parameter G(L12_FCC,AL,NI:AL;0) 298.15 6*U1ALNI; 6000 N !
Parameter G(L12_FCC,AL,NI:NI;0) 298.15 6*U1ALNI; 6000 N !

```

Figure 4.2: Partial database of the Al-Ni binary system showing the typical TDB format.

The description of each phase starts with the key word **Phase** followed by the phase name. The “%” separates the phase name from the phase description, that is, from information about sublattices. If the phase has other features than the sublattices that need to be described, such as magnetic or disordered contributions, then the symbol defined in the **Type_Definition** should directly follow % without any space in between (see the section that defines the L12_FCC phase in Figure 4.2). If this phase has no such additional feature, then there should be a space after %.

The LIQUID phase in Figure 4.2 is described as a substitutional solution phase. The first “1” after % indicates that the phase has one sublattice and the second “1” means the fraction of this sublattice is 1. The next line, which starts with the keyword “**Constituent**”, defines the constituents of each sublattice. After the phase name, the constituents in each sublattice are specified with a colon (“:”) separating the sublattices. A comma is used to separate species within the specification of a sublattice. A percent sign can be appended to the constituent symbol to indicate that it is a major constituent of this sublattice.

After the Constituent line, the model parameters follow.

The first two Parameter lines for the LIQUID phase represent the reference state. The next three lines define the excess Gibbs energy terms. For more information, see section 4.3.2. In Figure 4.2, the Gibbs energy of LIQUID (J/mol) is:

$$G_{LIQUID} = x_{Al} * GLIQAL + x_{Ni} * GLIQNI + RT(x_{Al} \ln x_{Al} + x_{Ni} \ln x_{Ni}) + x_{Al} x_{Ni} [(-197088 + 30.353 * T) + 5450(x_{Al} - x_{Ni}) + (54624 - 11.383 * T)(x_{Al} - x_{Ni})^2]$$

Note that the functions *GLIQAL* and *GLIQNI* are defined in the [Function](#) section and can thus be directly used in the Gibbs energy expressions.

The phase following LIQUID in Figure 4.2 is AL3NI1. This phase has two sublattices. The fraction of the first sublattice is 0.75 and the fraction of the second is 0.25. The second line specifies that AL occupies the first sublattice and that NI occupies the second sublattice. The Parameter line gives the Gibbs energy of AL3NI1 (J/mole atoms) as:

$$G_{AL3NI1} = 0.75 * GHSERAL + 0.25 * GHSERNI - 40463 + 5.312 * T$$

The third phase in Figure 4.2 is AL3NI2. For this phase, the stoichiometries (rather than the fractions) of its three sublattices are specified as 3, 2 and 1, respectively. These stoichiometries are given in moles, which means that the AL3NI2 definition concerns a phase with six moles of atoms. Hence, the Parameters listed below specify the Gibbs energy of six moles of atoms of this phase. The [Constituent](#) line specifies that AL occupies the first sublattice, AL and NI occupy the second sublattice and NI and vacancy (VA) occupy the third sublattice. AL3NI2 is an ordered intermetallic phase. Its Gibbs energy is described by the Compound-Energy Formalism. In the phase definition, a comma is used to separate species in the same sublattice, whilst a colon is used to separate species belonging to different sublattices. The following [Parameter](#) lines give the Gibbs energy of six mole atoms of AL3NI2 as:

$$G_{AL3NI2} = y_{Al}^I y_{Al}^{II} y_{Ni}^{III} (-41219 + 2.792 * T + 5 * GBCCAL + GBCCNI) + y_{Al}^I y_{Ni}^{II} y_{Ni}^{III} (-428055 + 71.808 * T + 3 * GBCCAL + 3 * GBCCNI) + y_{Al}^I y_{Al}^{II} y_{Va}^{III} (30000 - 3 * T + 5 * GBCCAL) + y_{Al}^I y_{Ni}^{II} y_{Va}^{III} (-356836 + 66.079 * T + 3 * GBCCAL + 2 * GBCCNI) + y_{Al}^I y_{Al}^{II} y_{Ni}^{III} (-38157) + y_{Al}^I y_{Al}^{II} y_{Ni}^{III} y_{Va}^{III} (-38157) + RT[3 * (y_{Al}^I \ln y_{Al}^I + 2 * (y_{Al}^{II} \ln y_{Al}^{II} + y_{Ni}^{III} \ln y_{Ni}^{III})) + (y_{Ni}^{III} \ln y_{Ni}^{III} + y_{Va}^{III} \ln y_{Va}^{III})]$$

Note that since AL is the only species that occupies the first sublattice, $y_{Al}^I = 1$ in the previous equation.

The DISORDER phase definition is actually part of the definition of [Phase L12_FCC](#). This is evident from the fact that the phase name L12_FCC is followed by %N. In the Type_Definition, "N" is defined so that it can be used to specify that L12_FCC has a disordered contribution from DISORDER. The Gibbs energy of L12_FCC (J/mole atoms) is written as:

$$G_{L12FCC} = [G_{L12Ord}(y_i^S) - G_{L12Ord}(y_i^S = x_i)] + G_{DISORDER}$$

For the L12_FCC phase in Figure 4.2, we have:

$$G_{L12Ord} = y_{Ni}^I y_{Al}^{II} (3 * U1ALNI) + y_{Al}^I y_{Ni}^{II} (3 * U1ALNI) + y_{Al}^I y_{Ni}^I y_{Al}^{III} (6 * U1ALNI) + y_{Al}^I y_{Ni}^I y_{Ni}^{III} (6 * U1ALNI) + RT[0.75 * (y_{Al}^I \ln y_{Al}^I + y_{Ni}^I \ln y_{Ni}^I) + 0.25 * (y_{Al}^{III} \ln y_{Al}^{III} + y_{Ni}^{III} \ln y_{Ni}^{III})]$$

$$G_{DISORDER} = x_{Al} GHSERAL + x_{Ni} GHSERNI + x_{Al} x_{Ni} (-16367 + 12U1ALNI) + RT(x_{Al} \ln x_{Al} + x_{Ni} \ln x_{Ni})$$

Other quantities, such as magnetic transition temperature, Bohr magnetons, molar volume or compressibility, can be described in a TDB file. However, while the TDB format can be used with several software packages, such as Thermo-Calc and PANDAT, there are minor differences in how the TDB files are interpreted by the different software. For example, PANDAT uses some additional key words and Property names in TDB files. Figure 4.3 shows an example of a TDB file that contains the PANDAT-specific key word **Optimization** to define a variable that is to be optimised. Following this key word is the variable's name, its lower limit, initial value and upper limit. Additional property parameters, such as Molar Volume (VM), Activation Energy (ACTIVATIONENERGY) and Surface Tension (SURFACETENSION) can be defined in a PANDAT-specific TDB file:

```

Element      AL          FCC_A1    26.982    4540     28.3 !
Element      VA          VACUUM    0         0         0 !
Element      ZN          HCP_A3    65.39     5657     41.63 !

Optimization LO 0 10465.55; 20000 N !
Optimization LOT -10 -3.39259; 0 N !

Phase LIQUID % 1 1 !
Constituent LIQUID :AL,ZN:!
Parameter G(LIQUID,AL;0) 298.15 G_AL_LIQUID; 6000 N !
Parameter G(LIQUID,ZN;0) 298.15 G_ZN_LIQUID; 6000 N !
Parameter G(LIQUID,AL,ZN;0) 298.15 LO+LOT*T; 6000 N !

Parameter VM(LIQUID,AL;0) 298.14 1.02E-005+1.12E-009*T; 2000 N !
Parameter VM(LIQUID,ZN;0) 298.14 1.92E-005+2.43E-009*T; 2000 N !

Parameter ACTIVATIONENERGY(LIQUID,AL;0) 298.14 20340+22.5*T; 2000 N !
Parameter ACTIVATIONENERGY(LIQUID,ZN;0) 298.14 6437+25.8*T; 2000 N !

Parameter SURFACETENSION(LIQUID,AL;0) 298.14 1.1-1.6E-4*T; 2000 N !
Parameter SURFACETENSION(LIQUID,ZN;0) 298.14 0.4161-7E-5*T; 2000 N !

```

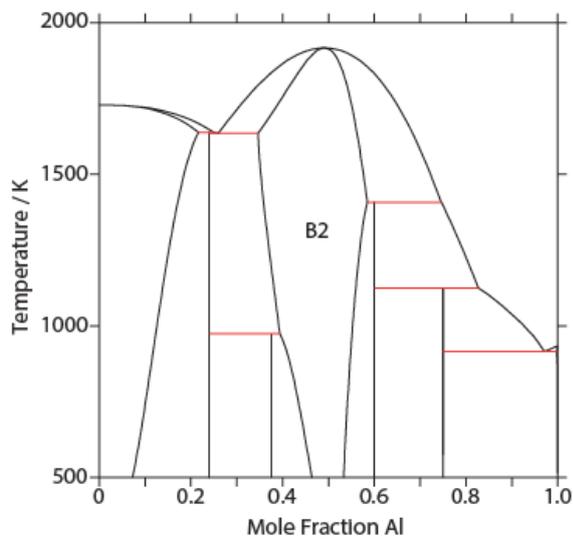
Figure 4.3: A TDB file with PANDAT-specific key words

4.4.10. Extensions

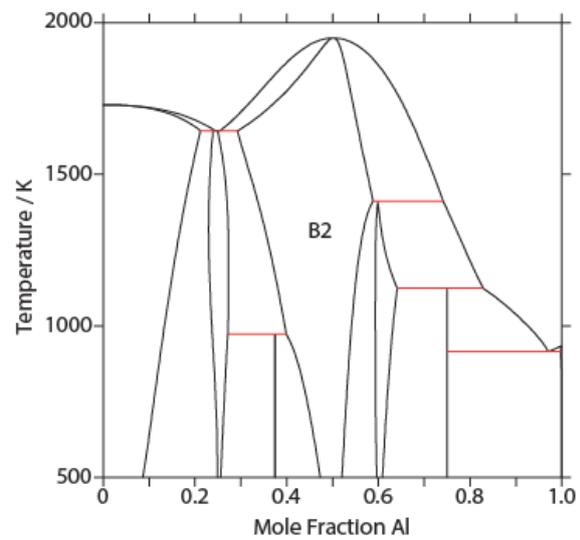
Initially, the CALPHAD (Calculation of Phase Diagrams) method was established as a tool for treating thermodynamics and phase equilibria of multicomponent systems. Since then, the method has been successfully applied to diffusion mobilities in multicomponent systems, creating the foundation for simulation of diffusion processes in these systems. In principle it should be possible to describe temperature, pressure and composition dependence of any phase specific property using the CALPHAD approach. Recently, the CALPHAD method has been expanded to other phase-based properties, including molar volumes and elastic constants, and has the potential to treat electrical and thermal conductivity and even two-phase properties, such as interfacial energies. The calculation of some of these quantities has already been implemented in a number of software. The general challenge for describing these properties is that, unlike the thermochemical quantities, most of them can be anisotropic depending on the crystal system of the phase. Although it will be sufficient to use an average value for the specific property for treating the bulk, this not adequate for the treatment of textured or thin film materials.

The suitability of the CALPHAD method for modelling diffusion processes was recognized early on. The underlying hypothesis is that diffusion in a crystalline phase with an equilibrium vacancy concentration occurs by a vacancy exchange mechanism. The phenomenological diffusion coefficients are then expressed in terms of a diffusion mobility function and a thermodynamic factor. The thermodynamic factor is determined using an existing multicomponent thermodynamic CALPHAD database. The conjecture is that the thermodynamic factor has the strongest composition dependence and provides the correct behaviour of the multicomponent off-diagonal diffusion

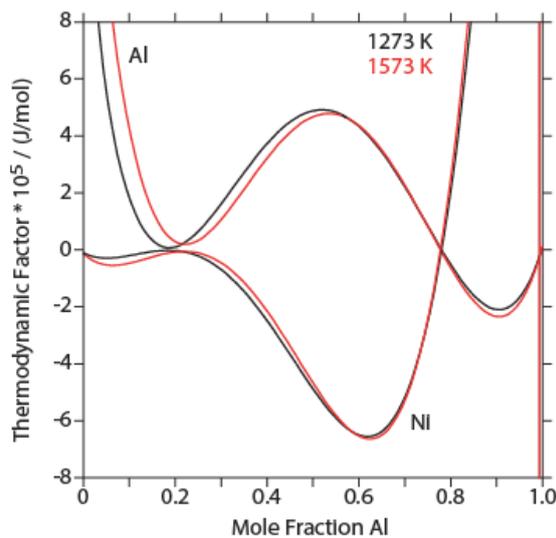
coefficients. Because of this linkage, it is imperative that the thermodynamic model reflects the phase as closely as possible. For example, ignoring the occurrence of structural vacancies of a phase will be detrimental to an accurate description of the diffusivities in this phase. This is illustrated in Figure 4.4 for the B2 phase of the Ni-Al system. In Figure 4.4(a) the phase is modelled as a simple substitutional solution [ref16] and in Figure 4.4(b) with the sublattice model taking into account the structural vacancies that occur on the Al-rich side of this phase [ref1]. Although both models reproduce the phase diagram, the effect on the thermochemical factor, Figure 4.4(c) and Figure 4.4(d), is pronounced. For the same reason, the composition dependence of the diffusion mobilities [ref5] are modelled with the same model as the thermodynamics. Results from calculations with both models are shown for the tracer and chemical diffusivities in Figure 4.4(e) and Figure 4.4(f), respectively.



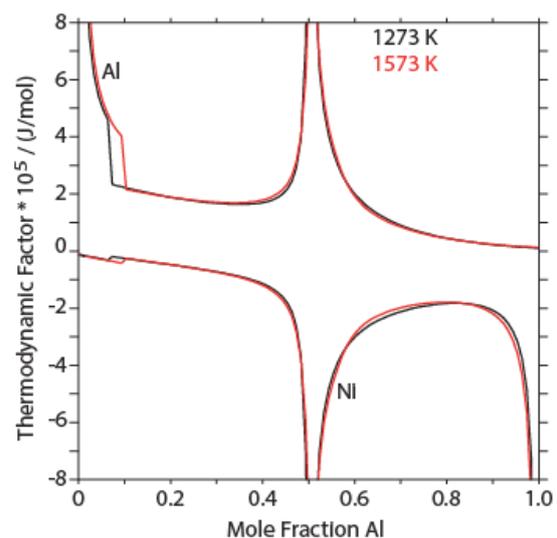
a



b



c



d

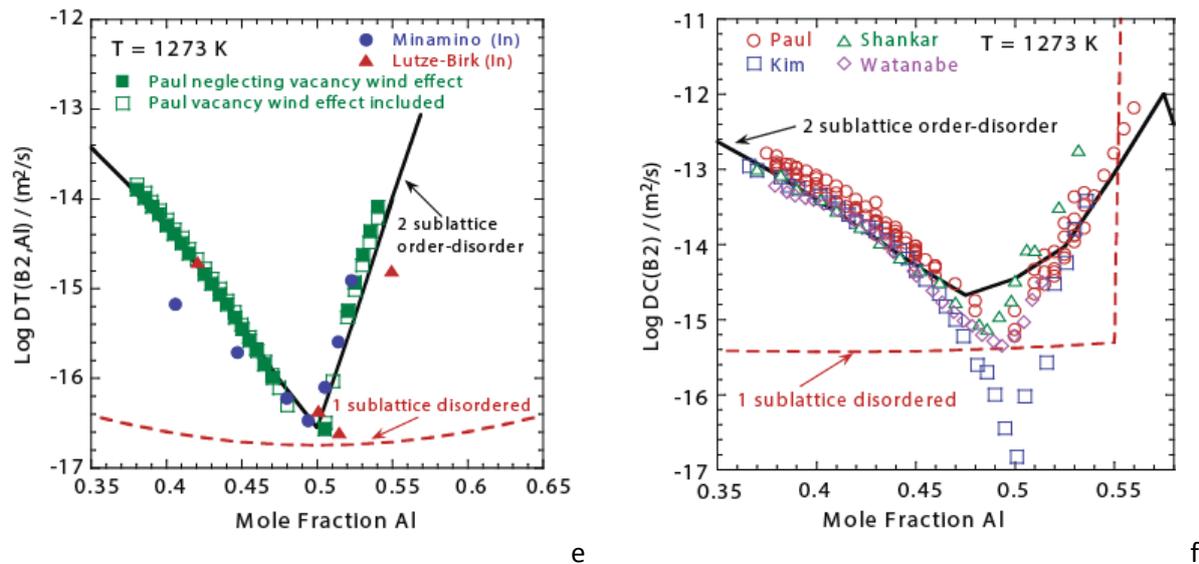


Figure 4.4: Model selection and diffusion modelling using a one sublattice substitutional model (a,c) and a two sublattice model considering structural vacancies (b,d) for the B2 phase in the Ni-Al system. (a,b) Phase diagram, (c,d) thermodynamic factor, (e) tracer and (f) chemical diffusivities using both models. Diffusion data are referenced in Campbell [ref5].

Use of the CALPHAD method to develop diffusion mobility databases has become essential in numerical simulations of diffusion processes for multicomponent alloys where composition and temperature dependent diffusion coefficient matrices are needed for each point after each time step. These simulations are carried out using a finite difference method (FDM), finite element method (FEM) or the phase field method. The diffusion simulation codes are linked via software libraries or are directly linked to the thermodynamics code. For example, the FDM code DICTRA is built on top of the thermodynamics code Thermo-Calc while the FDM phase field code MICRESS is linked via a software library to the same thermodynamics code. Most of the thermodynamics CALPHAD software has a module for the assessment of the thermodynamic model parameters, however, only a few are available for the assessment of diffusion mobilities, namely DICTRA and Pandat.

Although molar volume and bulk modulus or the elastic constants are parameters needed for the description of the pressure dependence of the Gibbs energy, descriptions of these quantities have been added only fairly recently to CALPHAD type databases and are only available for a few base elements. Consistent description of these quantities will result in equation of state descriptions of a phase as function of composition.

In addition to thermodynamics and diffusion mobilities, the CALPHAD method can also be applied to the description of thermal conductivity, electrical conductivity, optical properties such as refraction and reflectivity, viscosity and plasticity including dislocation migration energies. In metallic phases, where the heat is conducted by electrons, thermal and electrical conductivity are connected via the Wiedemann-Franz law. In insulator phases, where the heat is conducted by phonons, the thermal conductivity is linked to heat capacity and density. However, models for the description of these properties within the framework of the CALPHAD method still need to be developed.

For realistic modelling of microstructure evolution and properties, inter-phase properties are needed in addition to the properties of the individual phases. Examples of the needed inter-phase quantities are surface tension, interfacial energies and grain boundary diffusion. The surface tension of liquid

alloys can be derived from the thermodynamic quantities of the liquid using Butler's equation. Interfacial energies are important for the simulation of precipitation and coarsening processes. Currently most simulation tools for these processes use composition independent interfacial energies due to the lack of sufficient data collection. Although reasonable estimates can be obtained using thermodynamic approaches for composition dependent interfacial energies, it may be desirable to obtain these quantities from first principles approaches. Several models are available to evaluate nucleation rates from the thermodynamics and additional input parameters and have been implemented in precipitation calculation software. Grain boundary diffusion has been modelled using an approach similar to the one used for bulk diffusion.

Although the CALPHAD method has great potential for the description of properties beyond thermodynamics and diffusion mobilities, the development of models for use within the CALPHAD framework is still in its infancy.

4.4.11. Limitations and challenges

The CALPHAD method is well established for the modelling of the phase relationships and diffusion processes in multicomponent, multi-phase alloys and has been extensively used for alloy and process development. Although the method is powerful in predicting the properties of systems with more than three components, it is not a truly predictive method. The prediction of the properties of a multicomponent system is based on the extrapolation of the descriptions of the constituent binary and ternary systems. Information on the phases, phase boundaries and thermochemical quantities is needed for the development of the CALPHAD descriptions of these constituent systems. These data are mostly experimental data which are supplemented by data from first principles calculations (*ab initio*), especially where they are lacking or cannot be determined by experiments, such as the quantities of the hypothetical end-member phases needed for the CEF. If the occurrence of a phase is not known from experiments or predictions from first principles calculations, it cannot be predicted with the CALPHAD method. However, advances in first principles calculations and classic atomistic simulations have made it possible to obtain most of the needed information.

The two major challenges the CALPHAD method is facing are the development of models and databases for the description of other phase-based and inter-phase properties and the development of verification and validation methods.

Development of models and databases for other properties is essential for the application of the CALPHAD method beyond its initial use for evaluating whether a candidate alloy composition would produce the desired phases and avoid unwanted phases at the temperatures of interest and for selecting a temperature regime for processing. Combining results from CALPHAD calculations with models for other important alloy characteristics, such as creep resistance, castability and cost, allows for computational testing of thousands of candidate alloy compositions and the selection of a few promising candidate alloys for experimental evaluation. The CALPHAD calculations can be implemented in systematic searches using, for example, a genetic algorithm or mesh-adaptive direct search algorithm to find new candidate alloy compositions.

CALPHAD calculations using the same models and parameters and the same external conditions with different software should give the same results if the criteria for convergence are similar. It should be noted here that uncertainty of results from the CALPHAD calculations depend on the databases used and how reliably the original experimental data used in the development of these databases are reproduced. Currently, no method for uncertainty quantification of the results from a CALPHAD

database is available. The reliability of the results is most commonly expressed by plotting experimental data versus calculated results under the same conditions. If experimental information is lacking and data are supplemented with results for DFT calculations, differences of a few kJ/mol in these DFT energies can produce topologically different phase diagrams with phases that appear/disappear as stable ones depending on the input dataset used. Similar effects can be obtained if different sets of optimised CALPHAD parameters are obtained from experimental data after weighting individual data sets differently. Mathematical methodologies to better evaluate such uncertainties are desirable but challenging (if at all possible). The first logical step towards verification of CALPHAD descriptions is to perform a sensitivity analysis of the model parameters that are being adjusted during the optimisation of the thermodynamic description of a binary or ternary system. In addition to uncertainty quantification, it is desirable to develop a set of test cases to ensure that the results are consistent with accepted codes. Although the results from calculations should agree once the convergence criteria are fulfilled, it is not always guaranteed that the true set of equilibrium phases has been found. Development of protocols for the validation of CALPHAD software would provide additional assurance of the reliability of the results from CALPHAD calculations.

4.5. Deriving thermodynamics from *ab initio* calculations

Ab initio calculation of various thermodynamic data has developed impressively in recent years. More and more scientists are able to perform calculations and these calculations require less and less computing time. This means that an incredible number of calculated data have become widely available recently.

For thermodynamic modelling, in particular done in the frame of the CALPHAD method, calculated data can be used in the same way as experimental information. Among first-principles approaches, the Density Functional Theory (DFT) is able to find the ground state energy of a given compound with known structure and composition, which allows one to calculate its heat of formation at 0 K. Moreover, with additional statistically-derived approaches, the mixing enthalpy of disordered solid solution can be calculated. Furthermore, the phonon calculation yields vibrational contribution (entropy, heat capacity...) and allows one to estimate energetic stability at a finite temperature.

After a short introduction of the DFT methodology, the different thermodynamic properties that can be obtained by *ab initio* calculations will be detailed. More about DFT and other models at the electronic, atomistic and mesoscopic scales is found in chapter 5 of this book.

4.5.1. DFT methodology

DFT is among the most widely used methods in condensed-matter physics and computational chemistry, and has played a significant role in the development of new materials. This is not only due to the increasing performance of supercomputers, but also, and perhaps mainly, due to the availability of relatively inexpensive high performance workstations.

Consider an ordered and periodic compound with a known crystallographic structure and element distribution in the lattice. Its electronic structure results from a many-electron problem (n ions, N electrons) which cannot be solved analytically. A first theorem states that the ground state properties of this system are uniquely determined by an electron density ρ that in turn depends on only three spatial coordinates. Basically, the theorem reduces the many-body problem of N electrons

with 3N spatial coordinates to only three variables. This is achieved through the use of functionals of the electron density. The ground state energy is then obtained by minimising $E[\rho]$:

$$E[\rho] = \underbrace{K[\rho] + U[\rho]}_{F[\rho]} + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

where $K[\rho]$ is the kinetic energy, $U[\rho]$ the electron-electron interaction and V_{ext} the electron-ion interaction.

Because of the electron-electron interaction, $K[\rho]$ cannot be directly expressed. It has therefore been suggested that one should first, as an estimation, consider an auxiliary non-interacting system in order to solve the so-called mono-orbital Kohn–Sham equation:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{ext} + V_H + V_{XC} \right] \psi_i = \epsilon_i\psi_i,$$

where V_H is the Hartree contribution describing the electron-electron Coulomb repulsion, and V_{XC} is the so-called exchange-correlation potential. All the unknown many-body electron-electron interactions are now gathered in this latter term. This means that the accuracy of the DFT results heavily depends on the choice of the XC functional. V_{XC} can be expressed by the LDA (local density approximation), where it is assimilated to the energy of a homogenous electron gas of a density $\rho(r)$. The GGA (generalized gradient approximation) which includes the density and its first derivative is considered to be better for systems including strong variation of electronic density.

The Kohn-Sham equations can be solved by a self-consistent resolution done automatically in many available codes. Some of these codes, such as WIEN2K for example, take an all-electron description into account. These are called “full-potential” codes. Other codes, such as VASP, Quantum-Expresso or Abinit, use “pseudo potentials”. The Kohn-Sham equations are solved using the only valence electrons in a pseudo potential generated by the frozen core electrons and the nucleus contributions. By using plane waves as the basis set, a pseudo-potential approach can be very efficient and fast.

4.5.2. Heat of formation

Enthalpies of formation of a given compound are easily obtained from the difference between its calculated total energy and the sum of the weighted energies of the constituting pure elements in their stable reference states. Where experimental data are lacking, these differences are of great interest for CALPHAD modelling and other computational techniques that depend on the availability of thermodynamic data. Besides carrying out one’s own calculations, it is also possible to use available databases with stored calculated results (see, for example, <http://oqmd.org/>, <https://materialsproject.org/> or <http://www.afloplib.org/>).

As an example, the experimental enthalpies of formation, the values assessed after thermodynamic modelling and the calculated heats of formation of ordered compounds in Mo-Pt system are compared in Figure 4.5. Note the tight fit between calculated values and experimental measurements, especially in the case of compounds close to their stoichiometric composition (MoPt_2 , B19). But the figure also shows that the calculated values and the experimental measurements differ for compounds that have a significant non-stoichiometry accommodated by

substitution or vacancy mechanism (A_{15} , $D_{0_{19}}$). For these compounds, the high-throughput approach used with large databases should be considered with care. As an alternative, one can simulate defects in the structure to obtain both the right composition and the corresponding enthalpy for these compounds. This can be achieved using different approaches such as supercells or SQS. One advantage of the high throughput approach can also be illustrated with the figure, namely that one can obtain predictions of stable ordered structure at low temperature, here on the Pt rich side ($MoNi_4$, Pt_8Ti).

Note that if the Kopp-Neumann rule applies (the heat capacity of a compound is an average of the heat capacity of the constituting elements), the enthalpies of formation of compounds are temperature-independent and the enthalpies of formation calculated at 0 K are still valid at high temperatures.

Finally, one of the most interesting contributions of DFT to CALPHAD modelling is the possibility to estimate the enthalpy of formation of metastable compounds (end-members in the sublattice model) for which empirical values are missing.

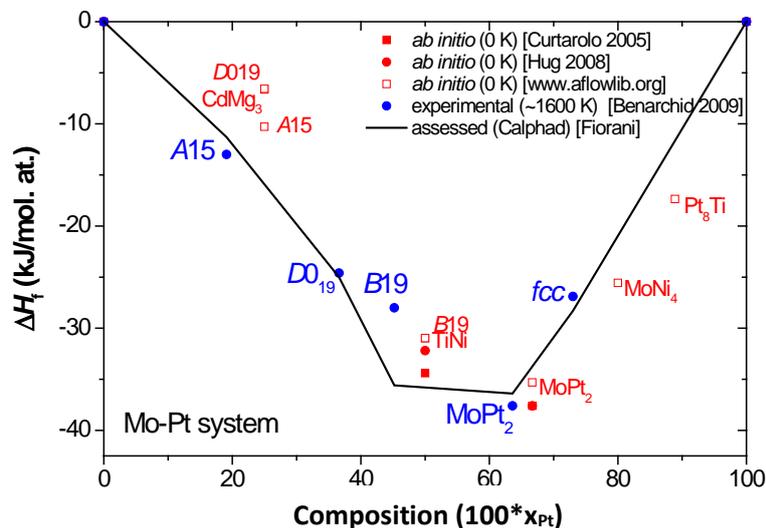


Figure 4.5: Experimental, thermodynamically assessed and DFT calculated enthalpies of formation in Mo-Pt system. (mole refers to one mole of atoms).

4.5.3. Mixing enthalpy

Contrary to what has been described above, not only ordered compounds but also disordered solutions can be calculated using DFT. Useful data such as enthalpies of mixing can be estimated by the Cluster Expansion Method (CEM) or by Coherent Potential Approximation (CPA). A simpler and more efficient approach has been developed in recent years: the Special Quasi-random Structure method (SQS). This consists of generating supercells with a limited number of atoms presenting neighbour correlation functions as close as possible to the ones in a fully random structure. For given compositions in the simplest structures (bcc , fcc , hcp), binary (16 atoms) and ternary (24 or 32 atoms), structures have already been generated and are available in the literature. For other compositions or other structures, dedicated tools are available to generate the SQS supercells (MCSQS in ATAT package).

As an example, Figure 4.6 shows the calculated mixing enthalpies in the bcc phase for two different systems (Mo-Nb and Cr-Fe) by CPA and SQS compared to experimental data. Close agreement

between calculated values and experimental measurements can be observed in both cases whatever the sign of the mixing enthalpy.

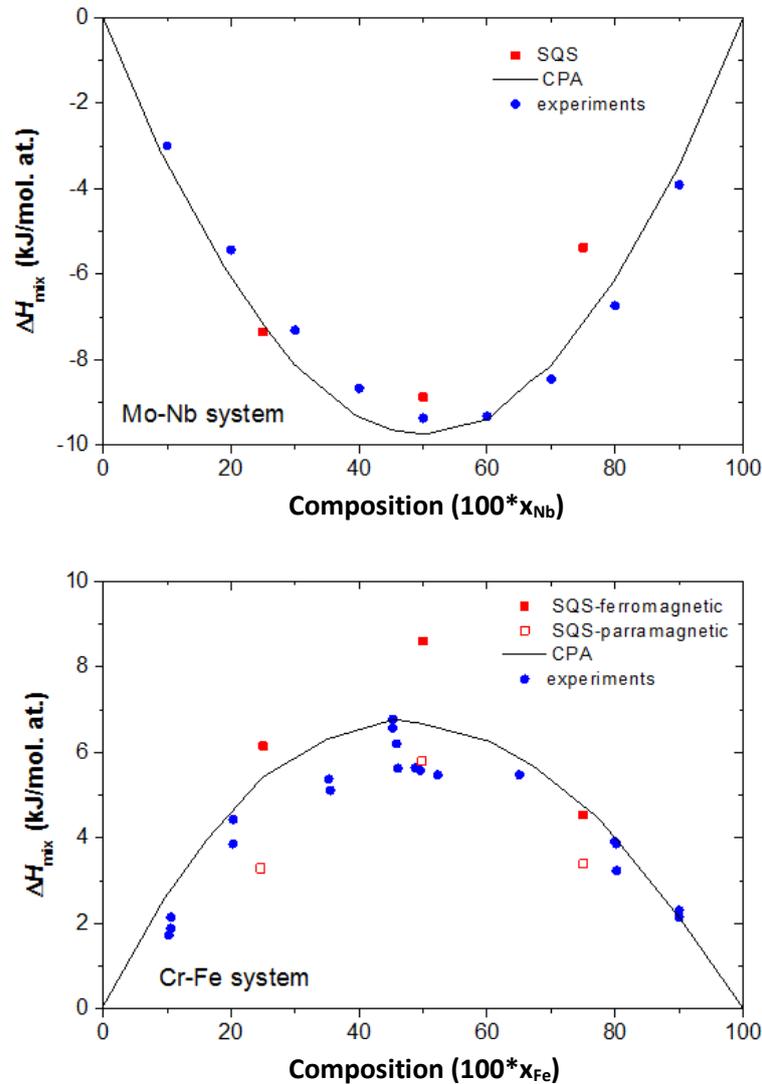


Figure 4.6: Experimental and calculated enthalpy of mixing in Mo-Nb and Cr-Fe bcc structure (redrawn from Jiang et al., Phys. Rev. B (2004)).

4.5.4. Lattice vibrations

DFT also allows for the calculation of force matrix in distorted structures, after slight atom movements have been imposed (Hellmann–Feynman theorem). This may be applied to the calculation of elastic or vibrational properties.

The phonon calculation can be numerically performed using different approaches: by perturbation theory (DFPT)/linear response methods or the supercell approach/direct method.

Two kinds of approximation may be used. In the harmonic approximation, the free energy is estimated at a constant volume. Its first derivative gives the vibrational entropy and its second derivative the heat capacity at constant volume. Using the quasi-harmonic approximation, the free

energy is expressed as a function of volume and allows one to obtain the C_p , thermal expansion and all the elastic moduli as a function of temperature.

Different codes are available to perform phonon calculations: Phonon, Phonopy, Phon.

Figure 4.7 presents a comparison of calculated and experimental elastic constants and bulk modulus as a function of temperature. Both data are important for a number of applications in ICME, in particular the extrapolations to temperatures where no experimental data can be measured. On the other hand, both C_p and vibrational entropy may be used in the frame of CALPHAD modelling.

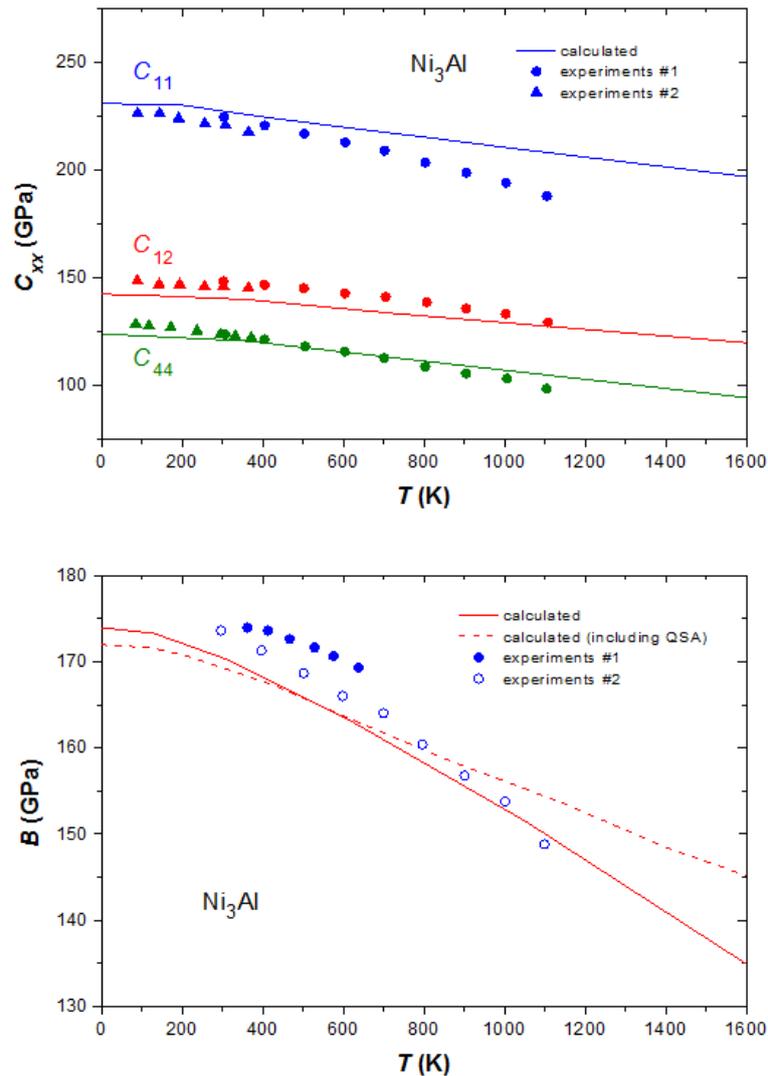


Figure 4.7: Experimental and calculated elastic constants and bulk modulus of Ni_3Al as a function of temperature (redrawn from Wang et al., *J. Phys. Condens. Matter* (2010)).

4.6. Use of thermodynamics at larger scales

Thermodynamics is the fundamental basis for essentially all phenomenological theories of materials, as well as mesoscale and continuum computational models of materials processes including phase transformations, chemical reactions, electronic and atomic/ionic transport and microstructure evolution. A complete thermodynamic description of a system, i.e. a fundamental equation of

thermodynamics, contains all the thermodynamic information of the system including not only the energies or free energies of all possible thermodynamic states but also all the equations of states as well as all the linear properties of the material such as heat capacity, thermal expansion coefficients, compressibility, etc. An example is the internal energy as a function of all extensive parameters such as entropy, volume or strain, number of moles of chemical species, surface/interface area, polarization, charge, magnetization, etc., $U(S, V \text{ or } e, N_1, N_2, \dots, N_n, A, Q, P, M, \dots)$. A fundamental equation more often used in practice is the Gibbs free energy as a function of temperature, pressure and/or stress, and extensive variables such as the number of moles of each species in the system, amount of surface area and others, i.e. $G(T, p, s, N_i, A, \dots)$. However, essentially all existing thermodynamic databases are mainly comprised of the Gibbs free energies of individual homogeneous phases as a function of temperature and composition under ambient or zero pressure while ignoring all other thermodynamic parameters. Therefore, the discussion on the use of thermodynamics in this section will tacitly assume that thermodynamic information means $G(T, x_1, x_2, \dots, x_n)$ for a multicomponent single-phase system. Although the main application of such thermodynamic functions is to obtain the phase equilibria of a given materials system, i.e. the equilibrium states of the system at different temperatures and compositions, this section will be focused on how such thermodynamic information can be used in theory and modelling of microstructure development. In addition to the Gibbs free energy function, this section will also outline what additional thermodynamic properties will be needed for a more complete description of microstructure stability and evolution, e.g. in computational microstructure models.

A microstructure refers to an inhomogeneous distribution of structural features that include phases of different compositions and/or crystal structures, grains of different orientations, domains of different structural variants or magnetizations, as well as structural defects such as interphase boundaries, grain boundaries, domain walls, cracks, surfaces and dislocations. For a more detailed discussion of the term microstructure please refer to chapter 3. The thermodynamic stability of a microstructure is determined by the total Gibbs free energy of a system, G , which may include the bulk chemical free energy density of each individual phase, the energies of defects, such as grain boundaries, surfaces, interfaces and dislocations, as well as the electrostatic, elastic and magnetic interaction energies. In a sharp-interface description, i.e. assuming the interfaces separating different phases or different domains within the same phase are mathematically sharp, a microstructure may be considered as a composite of individual single crystallites of different crystal structures/orientations/compositions and the interfaces between them. The total Gibbs free energy of a microstructure in this sharp-interface description can be written as

$$\text{Eq. -4.17} \quad G = \sum_{i=1}^p V_i g_i + \sum_{i=1}^q S_i \gamma_i + \sum_{i=1}^m L_i E_i^d + E_{elec} + E_{elast} + E_{mag}$$

where g_i is the bulk chemical free energy density of i^{th} phase with volume V_i , γ_i is the specific interfacial energy of i^{th} interface (grain boundary, surface or interphase boundary) with interfacial area S_i , E_i^d is the dislocation core energy per unit length of i^{th} dislocation with length L_i , and E_{elec} , E_{elast} and E_{mag} are the total electrostatic, elastic and magnetic energies, respectively. The molar Gibbs free energy (or chemical potential) as a function of temperature and composition for a phase from CALPHAD-types of databases can be directly converted to the free energy per unit volume.

In a diffuse-interface or phase-field description, the total free energy of an inhomogeneous microstructure in Eq. -4.17 is replaced by

Eq. 4-18

$$F = \int_V f_l^o dV + \int_V [f_l - f_l^o + f_g] dV + \int_V f_e dV$$

where f_l^o and f_l is the equilibrium and nonequilibrium local bulk chemical free energy densities that are functions of composition or phase-field variables, f_g is the gradient energy density and f_e represents the total energy due to elastic, electrostatic and magnetic long-range interactions.

Microstructure evolution takes place to reduce its total Gibbs free energy. The driving force could be the reduction in the bulk chemical free energy (the first term in Eq. 4-17), leading to the phase changes or transformations or chemical reactions. A phase transformation may lead to a change in the number of phases, e.g. a phase separation or decomposition reaction, or to a simple change of crystal structure for one of the phases to another with lower bulk chemical free energy density. A chemical reaction results in a change in chemical components and thus compositions. Therefore, the Gibbs free energies from thermodynamic databases can be used to determine the relative stability of possible thermodynamic states of a material system, and thus can be used quantify the thermodynamic driving forces for material processes such as phase transformations or chemical reactions under a given set of processing conditions.

The driving force for microstructure evolution can also be the reduction in the total interfacial energy (the second term in Eq. 4-17), leading to microstructure coarsening, i.e. the average spatial scale of domains, particles or grains in a microstructure increases as a function of time. In this case, the thermodynamic data necessary to model microstructure coarsening is the interfacial energy – grain boundary energy or interphase boundary energy or surface energy. Interfacial energy and its anisotropy are not only important in determining the morphologies of a particle, but also the driving force for microstructure coarsening. At finite temperatures, the change in grain boundary energy with temperature and the entropy contribution, mainly the vibrational entropy contribution, has to be included to obtain the interfacial free energy as a function of temperature. One useful approach to estimate interfacial energy is to use Gibbs free energy of a homogeneous system through the following expression,

Eq. 4-19

$$\sigma = 1/2 l \Delta f_{\max}$$

where l is the interfacial width and Δf_{\max} is the maximum difference between the nonequilibrium free energy as a function of composition and the equilibrium free energy of a two-phase mixture Figure 4.8.

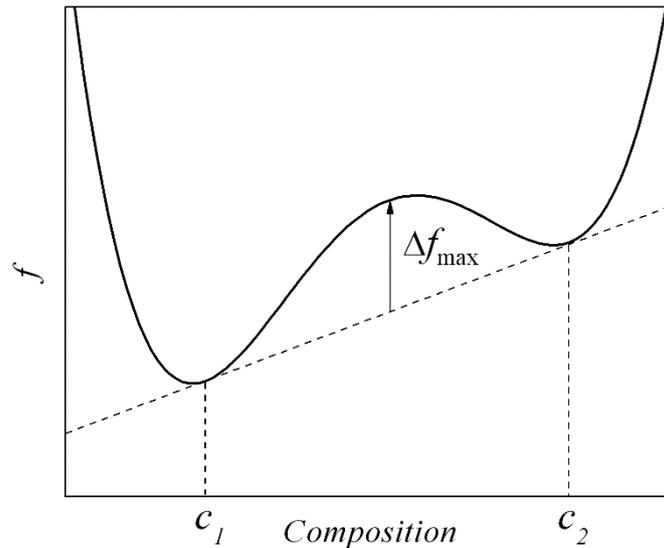


Figure 4.8: The schematic of free energy as a function of composition. Δf_{\max} is the maximum difference between the nonequilibrium free energy and the equilibrium free energy (the dashed common tangent).

In a solid microstructure, there can be local stresses generated which arise from strains produced due to thermal expansion coefficient mismatch between different phases in a microstructure or the lattice mismatch between new phases of a phase transformation and the parent phase or the lattice match among the different domains of the new phase. Different regions in a solid microstructure impose mechanical constraint on each other, and thus when the lattice parameters change in any region due to temperature or composition variations or due to a structural phase transformation, local elastic strains and stresses will develop. Microstructure will evolve to relax the total elastic strain energy and thus the total Gibbs free energy. The microstructure will also evolve under an applied stress field. For example, a ferroelastic domain wall, also called a twin wall, can be moved by an applied stress. Under a mechanical load, dislocations may also be generated and moved, i.e. a system may undergo plastic deformation, to release the strain or strain energy in a crystal. To model the strain- or stress-field microstructure evolution, the lattice parameters of individual phases as a function of temperature and composition is an important piece of information. Similar to the temperature dependence of lattice parameter of a material characterized by its thermal expansion coefficient, the composition dependence of lattice parameter is typically described by a composition expansion coefficient, $e_o = 1/a(da/dc)$. A constant or composition-independent e_o is typically referred to as the Vegard's law.

Microstructure changes can be driven by the reduction in electrostatic or magnetostatic interaction energies and the corresponding electric and magnetic fields. To incorporate these electric and magnetic contributions, the electric and magnetic properties will be necessary to compute the corresponding thermodynamic contributions, i.e. the electrostatic energy and the magnetic energy.

In summary, in order to predict the microstructure evolution of a materials system, it requires the information on the thermodynamic driving forces (Eq. -4.17) determined from the bulk free energy density for an individual phase, the interfacial (grain boundary, surface and interphase boundary) energies and lattice parameters and elastic constants of individual phases for obtaining the elastic energy density, as well as electrical and magnetic properties if electrostatics and magnetic materials are involved.

4.7. Applications and success stories

Until about the end of the first half of the 20th century, process and materials development had been based mostly on the knowledge of trends, basic concepts and extensive experimental programs. This route, as previously discussed elsewhere in this book, involves some intuition on the outcome of the process. However, several processes and materials defy, to some extent, the “extrapolations” based on intuition. The development of the argon–oxygen decarburisation (AOD) process in the 1970’s [app1][app2] and the development of the Sandvik-owned SAF 2507 duplex stainless steel in 1983 [app3] can be considered milestones in the use of modelling to support material and process development. Since then, computational thermodynamics has been an essential part of the toolbox in the design of stainless and specialty steel [app4][app5][app6][app7][app8]. Considerable progress has been made in process development by coupling thermodynamic models for liquid oxide slags and metal.

So-called “inclusion engineering” – engineered control of non-metallic inclusions in alloys – has emerged as a success story of the application of computational thermodynamics in steel processing by making it possible to design a proper slag for processing a given steel. For example, computational thermodynamics has been used to eliminate aluminates and spinel inclusions, and to minimize the content of alumina inclusions in bearing steels (such as 52100 or 100Cr6)[app9]. This involves simulating processing with slags of varying basicity (CaO/SiO_2), alumina and MgO contents, and evaluating the effects on the steel content of Ca, Mg, Al and O, for a given basic composition of Cr, C, Si and Mn. Figure 9 shows the calculated effect of varying the MgO content of a slag of constant basicity on the content of Al, O and Mg present in the steel. After performing equilibrium calculations for a range of compositions, a slag was selected and the actual results were compared with the calculated values. The agreement with respect to Al and O content is shown in Figure 4.10. Similar calculations are now routine for spring steel and tire cord steels [app10][app11]. The counterintuitive result that the basicity should be kept at lower values than usual for ladle metallurgy is an important result.

Similarly, the calculations of the amount of calcium to be added to liquid steel to prevent valve clogging and guarantee inclusion modification are now widely used [app12][app13][app14], eliminating the trial-and-error approach that was used until the end of the last century. Many reviews of various aspects of the application of the technique in steelmaking are available [app15][app16][app17]. Since many variables influence the clogging phenomena, various two-dimensional views are used to visualize the so-called “castability window”, i.e. the range of compositions in which low melting inclusions will be formed. Figure 4.11 is a particularly interesting way of presenting the data, since it strongly resembles the topology of the $\text{CaO-Al}_2\text{O}_3$ pseudo-binary diagram, classically used in the qualitative interpretation of clogging and inclusion modification. Currently, one of the challenges in inclusion modification and clogging prevention is the control of the process effectiveness during actual steelmaking so that corrections and process changes can be immediately performed. It was recently shown that by measuring soluble oxygen (which is an easy and rapid measurement on the shop floor with the use of disposable electrolytic cells), one can check the effectiveness of the process, even for Al killed steels [app18]. Figure 4.12 shows the results of several heats controlled in this way compared to the castability window calculated for the steel in question. The good agreement is evident.

Alloy design has also greatly benefited from the use of computational thermodynamics. This is true also in the case of the development and manufacture of “standard” products. The benefits of using microalloying in various steels have been optimised by computational thermodynamic techniques [app19][app20][app21], including simulations of precipitation in non-equilibrium conditions [app22]. For example, while designing a multi-phase flat steel for automotive applications, Murari, Costa e Silva and Avillez [app23] first simulated the possible effects of the main substitutional elements and of the interstitials carbon and nitrogen on the volume fraction and carbon content in the austenite present during intercritical treatment. To optimize the mechanical properties, the effects of boron additions were then studied.

Figure 4.13 shows the effect of the boron content on the austenite volume fraction at the intercritical temperature treatment of 820°C. The effect is shown as it was obtained by the three methods of computational thermodynamics, dilatometry and metallography of quenched specimens. The agreement of the results obtained by these methods is promising from the point of view of alloy design.

These and other examples of applications of computational thermodynamics can be found in the reports of the Ringberg meetings [app10][app24][app25]. They provide clear proof of the maturity of computational thermodynamics as a part of the ICME toolbox.

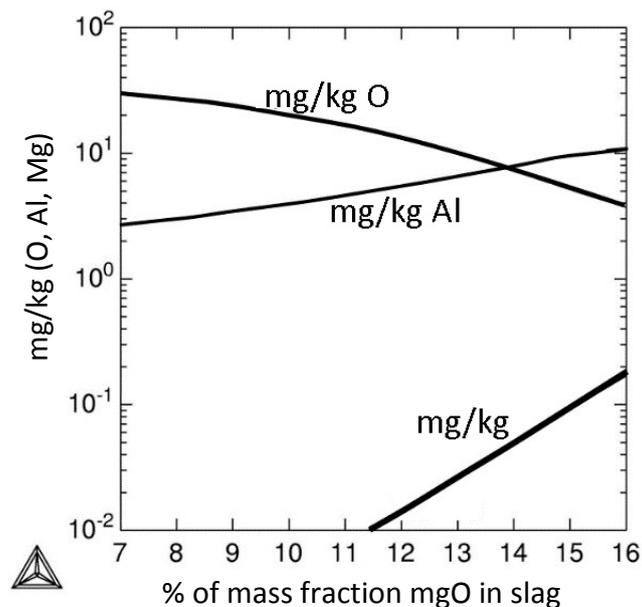


Figure 4.9: Effect of MgO in slag with constant Al₂O₃ and B=CaO/SiO₂ content on Al, O and Mg content in bearing steel in equilibrium with slag. Calculated with Thermo-Calc® and SLAG2 database at 1540°C.

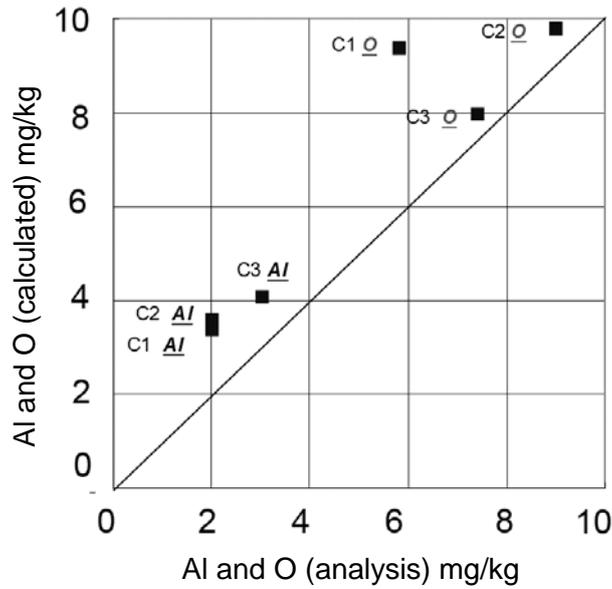


Figure 4.10: Comparison of calculated and measured Al and O content in bearing steel after ladle furnace processing. Calculated with Thermo-Calc® and SLAG2 database.

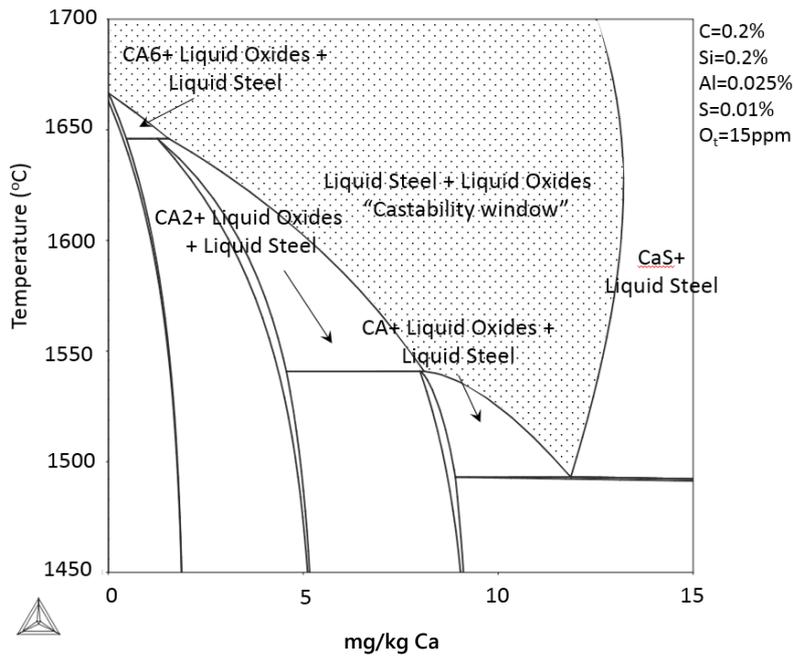


Figure 4.11: Temperature versus calcium content (mass fraction) diagram for a steel with the composition listed on the right top. The region where liquid inclusions are formed (the so called “castability window”) is clearly visible. The resemblance to the CaO-Al₂O₃ diagram makes it easier for the user to understand the results. Calculated with Thermo-Calc® and SLAG3 database.

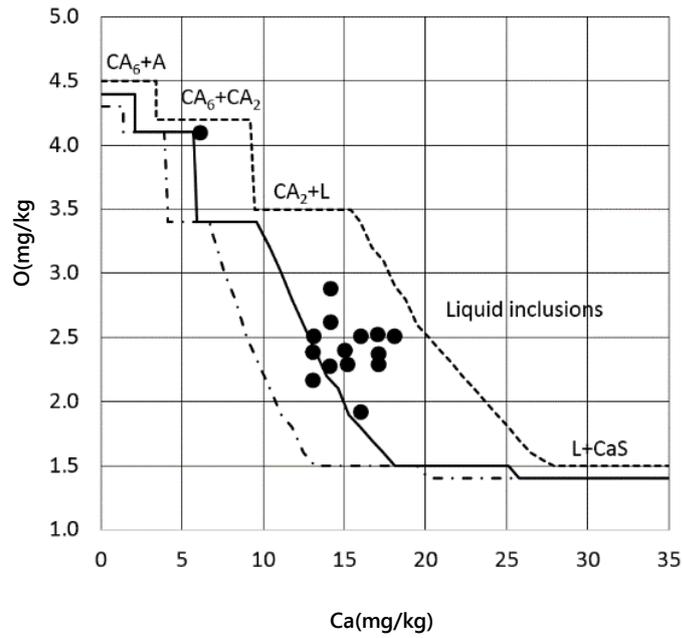


Figure 4.12: Calculated soluble oxygen in steel containing mass fraction of 0.025%Al, 0.01%S, and various values of O (15 mg/kg, 20 mg/kg and 30mg/kg, left to right) as a function of Ca content at 1540°C, compared with experimental measurements. Non-metallic phases present indicated for each region of composition. Calculated with Thermo-Calc® and SLAG3 database.

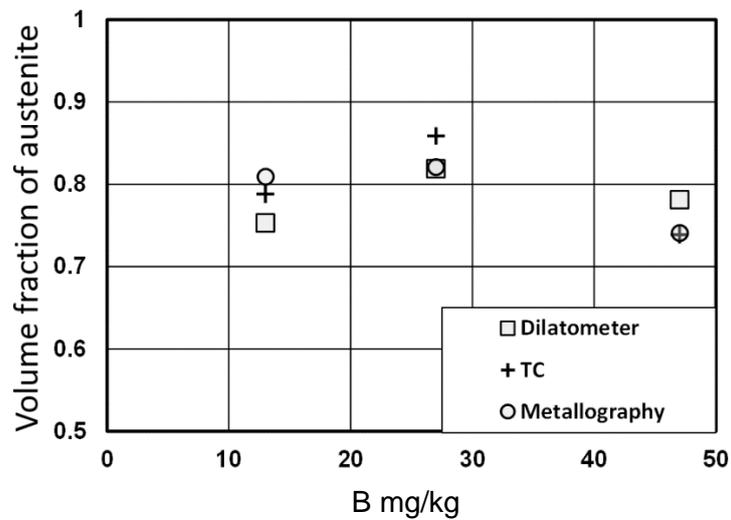


Figure 4.13: Comparison of the effect of Boron content on the volume fraction of austenite at intercritical heat treatment temperature of 820°C obtained by three different methods for a commercial multi-phase C, Mn, Si, Al, Nb, Ti, N, B steel. Calculations (TC) performed with Thermo-Calc® and TCFE6 database.

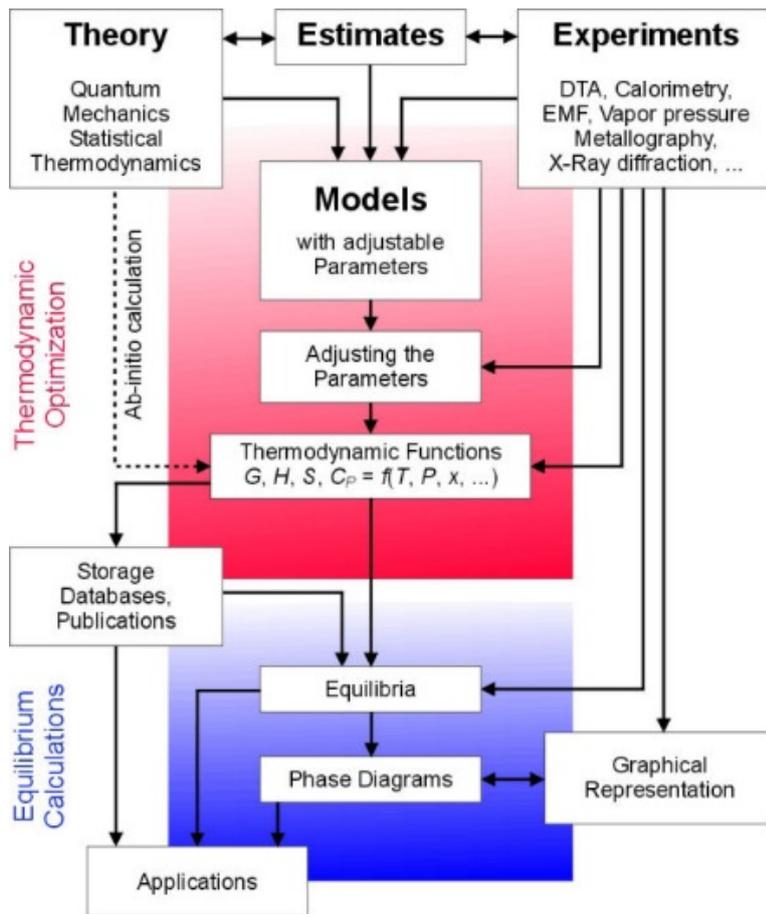


Figure 4.14 Diagram illustrating the CALPHAD methodology. By integrating the results of theoretical calculations and experiments, the adjustable model parameters are optimised and stored in databases (“Thermodynamic Optimization”). Using these databases, reliable phase diagrams can then be calculated (“Equilibrium Calculations”).

4.8. Software Tools

Table 4.4: Software tools and applications available for thermodynamic modelling

Name of code	Website	Type of code	Short description
Aspen Plus	www.aspentech.com/products/aspen-plus.aspx	Commercial	Chemical process optimisation software.
CaTCalc	https://staff.aist.go.jp/k.shobu/CaTCalc/	Commercial	Software that determines chemical thermodynamic equilibrium by the Gibbs Energy minimisation.
Chemical Equilibrium with	www.grc.nasa.gov/WWW/CEAWeb	Public domain	Calculates chemical equilibrium product concentrations from any set of reactants and determines thermodynamic and

Applications (CEA)			transport properties for the product mixture.
CHETAH	www.astm.org/BOOKSTORE/PUBS/DS51F.htm	Commercial	A resource for predicting both thermochemical properties and certain reactive chemical hazards associated with a pure chemical, a mixture of chemicals or a chemical reaction.
CP2K	http://www.cp2k.org/	Open Source	A program to perform atomistic and molecular simulations of solid state, liquid, molecular and biological systems.
CULGI	www.culgi.com	Commercial	A general purpose modelling platform including all relevant chemical modelling tools, from molecular representation to continuum level.
FactSage	www.factsage.com	Commercial	A fully integrated database computing system in chemical thermodynamics.
FluidProp	www.asimptote.nl	Commercial	A package for the calculation of fluid properties implementing advanced thermodynamic and transport models giving accurate and fast predictions.
Gemini	http://thermodata.online.fr/	Commercial	Software for thermochemical equilibria calculation by minimisation of the total Gibbs energy of the system under either constant pressure or volume conditions.
GEMS	http://gems.web.psi.ch/	Free for academia and research	Gibbs energy minimisation software for geochemical modelling.
gPROMS	http://www.psenteprise.com/gproms.html	Commercial	Platform technology for process modelling with a link to thermodynamic libraries.
HSC CHEMISTRY	www.outotec.com/en/Products--services/HSC-Chemistry	Commercial	Software designed for various kinds of chemical reactions and equilibria calculations as well as process simulation.
JMatPro	www.sentessoftware.co.uk	Commercial	Simulation software which calculates a wide range of materials properties for alloys and is particularly aimed at multi-component alloys used in industrial

			practice.
LAMMPS Molecular Dynamics Simulator	http://lammps.sandia.gov/	Open Source	A classical molecular dynamics code.
MatCalc	http://matcalc.tuwien.ac.at/	Commercial	A software project for computer simulation of phase transformations in metallic systems.
MegaWatSoft	www.megawatsoft.com	Commercial	Calculation of thermodynamic and transport properties of water and steam, carbon dioxide, ammonia and humid air.
MELTS	http://melts.ofm-research.org/		A software package designed to model phase (mineral, rock and liquid) relations during melting and crystallization.
MODELICA	https://www.modelica.org/		A non-proprietary, object-oriented, equation based language to conveniently model complex physical systems that may link to thermodynamic libraries.
MTDATA	www.npl.co.uk/science-technology/mathematics-modelling-and-simulation/mtdata	Commercial	A software tool for the calculation of phase equilibria and thermodynamic properties.
Multiflash	http://www.kbcatt.com/infochem-software/flow-assurance-software-multiflash	Commercial	Multiflash is a comprehensive PVT and physical properties package that allows for modelling and solving the phase behaviour of complex mixtures and pure substances.
OpenCalphad	www.opencalphad.com	Open Source	An informal international collaboration of scientists and researchers interested in the development of high quality software and databases for thermodynamic calculations for all kinds of applications.
Pandat	www.computherm.com	Commercial	An integrated computational tool developed on the basis of the CALPHAD (CALculation of PHase Diagram) approach for multi-component phase diagram calculation and materials property

			simulation.
Perple_X	www.perplex.ethz.ch		A thermodynamic calculation package suitable for rapidly creating phase diagrams of all types.
Simulis Thermodynamics	www.prosim.net	Commercial	A calculation server for thermophysical properties and phase equilibria calculations on pure components and mixtures.
THERMOCALC	www.metamorph.geo.uni-mainz.de/thermocalc		A thermodynamic calculation program that uses an internally-consistent thermodynamic dataset to undertake thermobarometry and phase diagram calculations for metamorphic rocks.
Thermo-Calc	www.thermocalc.com	Commercial	A powerful software package for the calculation of thermodynamic and phase equilibria. In conjunction with suitable thermodynamic databases, assessed using the CALPHAD approach, Thermo-Calc can be used for a wide variety of applications.
ThermoDataEngine (TDE)	http://trc.nist.gov/	Commercial	Provides critically evaluated thermodynamic and transport property data on demand using an expert system to extract data from the TRC Source data archive.
T-MATS	www.grc.nasa.gov/WWW/cdtb/software/t-mats.html	Open Source	A graphical thermodynamic simulation package built in MATLAB/Simulink (The MathWorks, Inc).
VMGSim	http://www.virtualmaterials.com/	Commercial	Process simulator for the oil, gas and chemical industries.

4.9. References and further reading

4.9.1. References

- [ref1] Ansara, N. Dupin, H.L. Lukas, B. Sundman, "Thermodynamic assessment of the Al-Ni system," *J. Alloy Compd.* 247 (1997) 20-30.
- [ref2] A.T. Dinsdale, "SGTE data for pure elements", *CALPHAD*, 15, 317–425(1991).

- [ref3] B. Sundman, X.-G. Lu, H. Ohtani, "The implementation of an algorithm to calculate thermodynamic equilibria for multi-component systems with non-ideal phases in a free software", *Comput. Mater. Sci.*, 101 (2015) 127–137.
- [ref4] Baroni, S.; Giannozzi, P. & Testa, A., Greens Function approach to linear response in solids, *Phys. Rev. Lett.*, 1987, 58, 1861. Article (Bar87)
- [ref5] C.E. Campbell, "Assessment of the diffusion mobilities in the γ' and B2 phases in the Ni-Al-Cr system," *Acta Mater.* 56 (2008) 4277-4290.
- [ref6] C. Tang, Y.-M. Sung, J. Lee, *App. Phys. Lett.* 100 (2012) 201903.
- [ref7] C. W. Bale et. al., *Calphad*, 26(2) (2002), p189-228.
- [ref8] C. W. Bale et. al., *Calphad*, 33 (2009), p295-311.
- [ref9] Gonze, X. & Lee, C., Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory, *Phys. Rev. B*, 1997, 55, 10355-10368. Article (Gon97)
- [ref10] H.L. Lukas, S.G. Fries, B. Sundman, *Computational Thermodynamics: The CALPHAD Method*, Cambridge University Press, Cambridge, UK, 2007.
- [ref11] J.G. Lee, H. Mori, J. Lee, T. Tanaka, K. Penttila, *JOM* 57 March (2005) 56-59.
- [ref12] J. Lee, J. Lee, T. Tanaka, H. Mori, *Nanotechnol.* 20 (2009) 475706.
- [ref13] J. Lee, J. Park, T. Tanaka, *Calphad* 33 (2009) 377-381.
- [ref14] J. Lee, K. J. Sim, *Calphad* 44 (2014) 129-132.
- [ref15] J. Lee, T. Tanaka, J.G. Lee, H. Mori, *Calphad* 31 (2007) 105-111.
- [ref16] J. Miettinen, "Thermodynamic description of the Cu-Ni-Al system at the Cu-Ni side," *Calphad* 29 (2005) 40-48.
- [ref17] J. Park, J. Lee, *Calphad* 32 (2008) 135-141.
- [ref18] K. Sim, J. Lee, *J. Alloy Comp.* 590 (2014) 140-146.
- [ref19] Kohn, W., *Nobel Lectures, Chemistry (1996-2000)* World Scientific Publishing, Singapore, 2003. Conference (Kohn)
- [ref20] Parlinski, K.; Li, Z. Q. & Kawazoe, Y., First-Principles Determination of the Soft Mode in Cubic ZrO_2
Phys. Rev. Lett., 1997, 78, 4063-4066. Article (Par97)
- [ref21] R. Schmid-Fetzer, D. Andersson, P.Y. Chevalier, L. Eleno, O. Fabrichnaya, U.R. Kattner, B. Sundman, C. Wang, A. Watson, L. Zabdyr, M. Zinkevich, "Assessment techniques, database design and software facilities for thermodynamics and diffusion", *CALPHAD*, 31, 38–52(2007).
- [ref22] Sanchez, J.M.; Ducastelle, F. & Gratias, D., *Generalized cluster description of multicomponent systems*, *Physica A*, 1984, 128, 334-350. Article (San84)
- [ref23] Sanchez, J., *Cluster expansion and the configurational theory of alloys*, *Physical Review B*, APS, 2010, 81, 224202. Article (San10)
- [ref24] T. Tanaka, S. Hara, *Z. Metallkd.* 92 (2001) 467-472.
- [ref25] T. Tanaka, S. Hara, *Z. Metallkd.* 92 (2001) 1236-1241.
- [ref26] Togo, A.; Oba, F. & Tanaka, I., First-principles calculations of the ferroelastic transition between rutile-type and $CaCl_2$ -type SiO_2 at high pressures, *Phys. rev. B*, 2008, 78, 134106. Article (Tog08)

- [ref27] van de Walle, A.; Tiwary, P.; de Jong, M.; Olmsted, D.; Asta, M.; Dick, A.; Shin, D.; Wang, Y.; Chen, L.-Q. & Liu, Z.-K., Efficient stochastic generation of special quasirandom structures, *Calphad*, 2013, 42, 13-18. Article (Wal13)
- [ref28] Zunger, A.; Wei, S. H.; Ferreira, L. G. & Bernard, J. E., *Special quasirandom structures*, *Phys. Rev. Lett.*, 1990, 65, 353. Article (Zun90)

4.9.2. Success stories

- [app1] W. A. Krivsky. The Linde Argon-Oxygen Process for Stainless Steels; A case study of Major Innovation in a Basic Industry. *Metall. Trans.* 1973;4(June):1439–47.
- [app2] N. Å. I. Andersson; A. Tillander; L. T. I. Jonsson; P. G. Jönsson, Fundamental decarburisation model of AOD process. *Ironmaking and Steelmaking*. 2013; 40(5): 390-397
- [app3] H. Widmark. Importance of Mats Hillert's research work on industrial applications. *Scand. J. Metall.* 1991;20:72–8.
- [app4] I. Calliari, M. Zanesco, E. Ramous. Influence of isothermal aging on secondary phases precipitation and toughness of a duplex stainless steel SAF 2205. *J Mater Sci.* 2006 Nov 27;41(22):7643–9.
- [app5] S. Wessman, L. Karlsson, R. Pettersson, A. Östberg. Computational Thermodynamics Study Of The Influence Of Tungsten In Superduplex Stainless Weld Metal. *Weld World*. 2012;56(11-12):79–87.
- [app6] G.B. Olson. Genomic materials design: The ferrous frontier. *Acta Mater.* 2013 Feb;61(3):771–81.
- [app7] S. Huth, N. Krasokha, W. Theisen. Development of wear and corrosion resistant cold-work tool steels produced by diffusion alloying. *Wear*. 2009 Jun;267(1-4):449–57.
- [app8] A. B. Farina et al. Use of thermodynamic modeling to the process optimization and development of new alloys (in Portuguese). *Tecnol Met Mater Min.* 2014;11(4):1–8.
- [app9] J. Monnot, B. Heritier, J.Y. Cogne. Inclusion Cleanness and Fatigue Resistance of Rolling Bearing Steels, *Rev. Metall. - CIT*, 1986; 83(10):761-770.
- [app10] A. Costa e Silva, J. Ågren, M.T. Clavaguera-Mora, D. Djurovic, T. Gomez-Acebo, B.-J. Lee et al. Applications of computational thermodynamics — the extension from phase equilibrium to phase transformations and other properties. *Calphad*. 2007 Mar;31(1):53–74.
- [app11] L. Holappa, S. Nurmi, S. Louhenkilpi, T. Antola. Thermodynamic Evaluation for Inclusion Formation in High Carbon and Spring Steels. 2007. "Clean Steel Conference 2007, Balatonfüred, Hungary.
- [app12] A Costa e Silva. Calcium and magnesium thermodynamics in steel and its impacts on secondary steelmaking: a computational thermodynamics approach. *Rev Metall - CIT*. 2008;105(4):181–93.

- [app13] L. Holappa, M. Hamallinen, M. Liukkonen, M. Lind. Thermodynamic examination of inclusion modification and precipitation from calcium treatment to solidified steel. *Ironmaking & Steelmaking*. 2003 Apr 1;30(2):111–5.
- [app14] L. Oertel, A. Costa e Silva. Application of thermodynamic modeling to slag-metal equilibria in steelmaking. *CALPHAD*. 2000;23(3-4):379–91.
- [app15] I.-H. Jung. Overview of the applications of thermodynamic databases to steelmaking processes. *Calphad*. 2010 Sep;34(3):332–62.
- [app16] A Costa e Silva. Application of computational thermodynamics to steelmaking and processing - Keynote Lecture. *Proceeding of the 19th IAS Steel Conference*. Rosario, Santa Fe, Argentina: IAS; 2013. p. 1–21.
- [app17] A Costa e Silva. Thermodynamic aspects of inclusion engineering in steels. *Rare Met*. 2006;25(5):412–9.
- [app18] M.Mercier. Dynamic CaSi addition (in Portuguese), M.Sc. Thesis, UFMG, Belo Horizonte, Brazil; 2014.
- [app19] S. Akamatsu, M. Hasebe , T. Senuma, Y. Matsumura, O. Akisue. Thermodynamic calculation of solute carbon and nitrogen in Nb and Ti added extra-low Carbon Steel. *ISIJ International*. 1994;34(1):9–16.
- [app20] K. Frisk. Thermodynamic modelling of multicomponent cubic Nb, Ti and V carbides/carbonitrides. *CALPHAD*. 2008 Jun;32(2):326–37.
- [app21] K. Inoue, N. Ishikawa, I. Ohnuma, H. Ohtani, K. Ishida. Calculation of Phase Equilibria between Austenite and (Nb, Ti, V)(C, N) in Microalloyed Steels. *ISIJ International*. 2001;41(2):175–82.
- [app22] R. N. Carvalho, A. Costa e Silva, R. Barbosa. Precipitation of carbonitrides in steels microalloyed with Nb and Ti during hot rolling of seamless tubes. *3rd International Conference on Thermomechanical Processing of Steels*, Padua, Italia: Associazione Italiana di Metallurgia, Rome; 2008.
- [app23] F.D. Murari, A Costa e Silva, R R Avillez. Effect of Boron on the microstructure and mechanical properties of cold rolled multiphase steels. *Program and Abstracts Book CALPHAD 2011*. Rio de Janeiro, Brasil: ABM; 2011. p. 121.
- [app24] U. Kattner, G. Erickson, P. Spencer, M. Schalin,R. Schmid-Fetzer,B. Sundman, et al. Report of Group 4 & 5: Process Modeling and applications- 1997 Ringberg Workshop. *CALPHAD*. 2000;24(1):55–94.
- [app25] J. Agren, F.H. Hayes, L. Höglund, U. Kattner, B. Legendre, R. Schmid-Fetzer. Applications of computational thermodynamics. *Z Metallkd*. 2002;93(2) 128-142.

4.9.3. Further Reading

1. C.E. Campbell, U.R. Kattner, Z.-K. Liu, "The development of phase-based property data using the CALPHAD method and infrastructure needs," *Integr. Mater. Manuf. Innov.* 3 (2014) 12.
2. Dove, M. T., *Introduction to lattice dynamics*, Cambridge University Press, New York, 1993.
3. G. Grimvall, "Thermophysical Properties of Materials," Enlarged and revised edition, Elsevier, Amsterdam, 1999.
4. J. W. Tester and M. M. Modell, *Thermodynamics and Its Applications (3rd Edition)*, Prentice Hall (1996)
5. Singh, D. J. & Nordstrom, L., *Planewaves, Pseudopotentials and the LAPW Method*, Springer US, 2006.
6. W. Gąsior, "Viscosity modelling of binary alloys: Comparative studies," *Calphad* 44 (2014) 119–128.
7. van de Walle, A.; Asta, M. & Ceder, G., *The alloy theoretic automated toolkit: A user guide*, *Calphad*, 2002, 26, 539-553.
8. van de Walle, A.; Tiwary, P.; de Jong, M.; Olmsted, D.; Asta, M.; Dick, A.; Shin, D.; Wang, Y.; Chen, L.-Q. & Liu, Z.-K., *Efficient stochastic generation of special quasirandom structures*, *Calphad* , 2013, 42, 13-18.
9. Series of papers from Ringberg Workshops on CALPHAD modelling: "Unary data for elements and other end-members of solutions," *Calphad* 19 (1995) 433-571; "Solution modelling," *Calphad* 21 (1997) 139-285; "Applications of computational thermodynamics," *Calphad* 24 (2000) 15-94; "Thermodynamic modelling and applications," *Z. Metallkd.* 92 (2001) 513-562, 93 (2002) 128-142; "Thermodynamic modeling and first-principles calculations," *Calphad* 31 (2007) 2-74; "Ringberg unary workshop 2013," *Phys. Status Solidi B* 251 (2014) 9-129.
10. H.L. Lukas, S.G. Fries, B. Sundman, *Computational Thermodynamics: The CALPHAD Method*, Cambridge University Press, Cambridge, UK, 2007.
11. N. Saunders, A.P. Miodownik, *CALPHAD,(Calculation of Phase Diagrams): A Comprehensive Guide*, Pergamon, Oxford, UK, 1998