

## Chapter 5

# Thermodynamic Models for Solution and Compound Phases

### 5.1. INTRODUCTION

Thermodynamic modelling of solution phases lies at the core of the CALPHAD method. Only rarely do calculations involve purely stoichiometric compounds. The calculation of a complex system which may have literally 100 different stoichiometric substances usually has a phase such as the gas which is a mixture of many components, and in a complex metallic system with 10 or 11 alloying elements it is not unusual for all of the phases to involve solubility of the various elements. *Solution phases* will be defined here as any phase in which there is solubility of more than one component and within this chapter are broken down to four types: (1) random substitutional, (2) sublattice, (3) ionic and (4) aqueous. Others types of solution phase, such as exist in polymers or complex organic systems, can also be modelled, but these four represent the major types which are currently available in CALPHAD software programmes.

For all solution phases the Gibbs energy is given by the general formula

$$G = G^{\circ} + G_{\text{mix}}^{\text{ideal}} + G_{\text{mix}}^{\text{xs}} \quad (5.1)$$

where  $G^{\circ}$  is the contribution of the pure components of the phase to the Gibbs energy,  $G_{\text{mix}}^{\text{ideal}}$  is the ideal mixing contribution and  $G_{\text{mix}}^{\text{xs}}$  is the contribution due to non-ideal interactions between the components, also known as the Gibbs excess energy of mixing.

The random substitutional and sublattice models are intimately related, as a phase with random occupation of atoms on all sites can technically be considered as a phase containing a 'single sublattice' and mathematically the same general equations used in both cases. However, it is useful to separate the two types as the sublattice models implicitly define some internal, spatial substructure and give rise to site occupations which define stoichiometric compounds. Also, and very importantly,  $G_{\text{mix}}^{\text{ideal}}$  and  $G_{\text{mix}}^{\text{xs}}$  are governed by site occupation of the components in the various sublattices rather than the global concentration of the components themselves.

This chapter will begin, very briefly, with the thermodynamic representation of Gibbs energy for stoichiometric compounds before concentrating on the situation when mixing occurs in a phase.

## 5.2. STOICHIOMETRIC COMPOUNDS

The integral Gibbs energy,  $G_{[T,P]}$ , of a pure species or stoichiometric compound is given simply by the equation

$$G_{[T,P]} = H_{[T,P]} - TS_{[T,P]} \quad (5.2)$$

where  $H_{[T,P]}$  and  $S_{[T,P]}$  are the enthalpy and entropy as a function of temperature and pressure. Thermodynamic information is usually held in databases using some polynomial function for the Gibbs energy which, for the case of the Scientific Group Thermodata Europe (Ansara and Sundman 1987), is of the form (Dinsdale 1991)

$$G_{m[T]} - H_m^{SER} = a + bT + cT \ln(T) + \sum_2^n d_n T^n \quad (5.3)$$

The left-hand-side of the equation is defined as the Gibbs energy relative to a standard element reference state (SER) where  $H_m^{SER}$  is the enthalpy of the element or substance in its defined reference state at 298.15 K,  $a$ ,  $b$ ,  $c$  and  $d_n$  are coefficients and  $n$  represents a set of integers, typically taking the values of 2, 3 and -1. From Eq. (5.3), further thermodynamic properties can be obtained as discussed in Chapter 6.

$$S = -b - c - c \ln(T) - \sum_2^n n d_n T^{n-1}$$

$$H = a - cT - \sum_2^n (n-1) d_n T^n$$

$$C_p = -c - \sum_2^n n(n-1) d_n T^{n-1}$$

Equation (5.3) is given with respect to temperature but other terms associated with pressure and magnetism can be added. The representation of such effects is described more completely in Chapters 6 and 8.

## 5.3. RANDOM SUBSTITUTIONAL MODELS

Random substitutional models are used for phases such as the gas phase or simple metallic liquid and solid solutions where components can mix on any spatial position which is available to the phase. For example, in a simple body-centred cubic phase any of the components could occupy any of the atomic sites which define the cubic structure as shown below (Fig. 5.1).

In a gas or liquid phase the crystallographic structure is lost, but otherwise positional occupation of the various components relies on random substitution rather than any preferential occupation of site by any particular component.

References are listed on pp. 124–126.

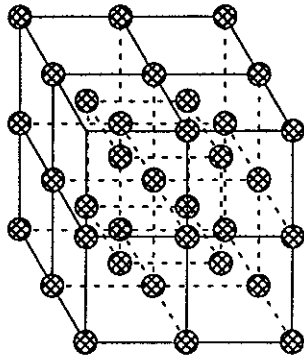


Figure 5.1. Simple body-centred cubic structure with random occupation of atoms on all sites.

### 5.3.1 Simple mixtures

**5.3.1.1 Dilute solutions.** There are a number of areas in materials processing where low levels of alloying are important, for example in refining and some age-hardening processes. In such cases it is possible to deal with solution phases by dilute solution models (Wagner 1951, Lupis and Elliott 1966). These have the advantage that there is a substantial experimental literature which deals with the thermodynamics of impurity additions, particularly for established materials such as ferrous and copper-based alloys. However, because of their fundamental limitations in handling concentrated solutions they will only be discussed briefly.

In a highly dilute solution, the solute activity ( $a_i$ ) is found to closely match a linear function of its concentration ( $x_i$ ). In its simplest form the activity is written as

$$a_i = \gamma_i^o x_i \quad (5.4)$$

where  $\gamma_i^o$  is the value of the activity coefficient of  $i$  at infinite dilution. This is known as Henry's law. Equation (5.5) may be rewritten in terms of partial free energies as

$$\bar{G}_i = \bar{G}_i^{xs} + RT \log_e x_i \quad (5.5)$$

where  $\bar{G}_i^{xs}$  has a constant value in the Henrian concentration range and is obtained directly from  $\gamma_i^o$ . The expression can also be modified to take into account interactions between the solute elements and Eq. (5.5) becomes

$$\bar{G}_i = \bar{G}_i^{xs} + RT \log_e x_i + RT \sum_j \epsilon_{ij}^j x_j \quad (5.6)$$

where  $x_i$  is the concentration of solute  $i$  and  $\epsilon_{ij}^j$  is an interaction parameter taking into account the effect of mixing of component  $i$  and  $j$  in the solvent. There are

various other treatments of dilute solutions, mainly associated with how secondary interactions are considered (Foo and Lupis 1973, Kirkaldy *et al.* 1978, Bhadeshia 1981, Enomoto and Aaronson 1985). Recently a more sophisticated dilute solution treatment consistent with the Gibbs–Duhem integration in more concentrated solutions has been put forward by Bale and Pelton (1990). This allows the solute range handled by dilute solution models to be expanded significantly.

Unfortunately, the dilute solution model is limited in its applicability to concentrated solutions. This causes problems for alloys such as Ni-based superalloys, high alloy steels, etc., and systems where elements partition strongly to the liquid and where solidification processes involve a high level of segregation. It is also not possible to combine dilute solution databases which have been assessed for different solvents. The solution to this problem is to use models which are applicable over the whole concentration range, some of which are described below.

**5.3.1.2 Ideal solutions.** An ideal substitutional solution is characterised by the random distribution of components on a lattice with an interchange energy equal to zero. The entropy due to configuration is easily calculated and is related to the probability of interchange of the components. The configurational entropy  $S^{\text{conf}}$  is given by

$$S^{\text{conf}} = k \log_e W_P \quad (5.7)$$

where  $k$  is Boltzmann's constant and  $W_P$  is the number of configurations in which the components can be arranged for a given state. For a multicomponent system  $W_P$  is equal to the number of permutations given by

$$W_P = \frac{N!}{\prod_i n_i!} \quad (5.8)$$

where

$$N = \sum_i n_i \quad (5.9)$$

$n_i$  is the number of components of  $i$  and  $N$  is the total number of components in the system. For one mole of components,  $N$  is equal to Avogadro's number. From Stirling's formula,  $S^{\text{conf}}$  is now equal to

$$S^{\text{conf}} = -k \sum_i n_i \log_e \frac{n_i}{N} \quad (5.10)$$

The ideal molar entropy of mixing is then given by

$$S_{\text{mix}}^{\text{ideal}} = -Nk \sum_i x_i \log_e x_i \quad (5.11)$$

where  $x_i$  is the mole fraction of component  $i$ . With the assumption that the interchange energy is zero it is possible to substitute the atoms without changing the energy of that state and  $G_{\text{mix}}^{\text{ideal}}$  is then given by

$$G_{\text{mix}}^{\text{ideal}} = -TS_{\text{mix}}^{\text{ideal}} = RT \sum_i x_i \log_e x_i \quad (5.12)$$

where  $R$  is the gas constant. The Gibbs energy of an ideal solution phase will then be

$$G_m = \sum_i x_i G_i^{\circ} + RT \sum_i x_i \log_e x_i \quad (5.13)$$

with  $G_i^{\circ}$  defining the Gibbs energy of the phase containing the pure component  $i$ . For the case of gases, ideal mixing is often assumed and this assumption can often be quite reasonable. However, in condensed phases there is always some interaction between components.

**5.3.1.3 Non-ideal solutions: regular and non-regular solution models.** The regular solution model is the simplest of the non-ideal models and basically considers that the magnitude and sign of interactions between the components in a phase are independent of composition. Assuming the total energy of the solution ( $E_0$ ) arises from only nearest-neighbours bond energies in a system  $A - B$  then

$$E_0 = \omega_{AA} E_{AA} + \omega_{BB} E_{BB} + \omega_{AB} E_{AB} \quad (5.14)$$

where  $\omega_{AA}$ ,  $\omega_{BB}$ ,  $\omega_{AB}$ ,  $E_{AA}$ ,  $E_{BB}$  and  $E_{AB}$  are the number of bonds and energies associated with the formation of different bond types  $AA$ ,  $BB$  and  $AB$ . If there are  $N$  atoms in solution and the co-ordination number for nearest neighbours of the crystal structure is  $z$ , the number of bond types being formed in a random solution is

$$\omega_{AA} = \frac{1}{2} N z x_A^2 \quad (5.15a)$$

$$\omega_{BB} = \frac{1}{2} N z x_B^2 \quad (5.15b)$$

$$\omega_{AB} = N z x_A x_B \quad (5.15c)$$

where  $x_A$  and  $x_B$  are the mole fractions of  $A$  and  $B$ . Substituting Eqs (5.15 (a–c)) into Eq. (5.14) gives

$$E_0 = \frac{Nz}{2} (x_A E_{AA} + x_B E_{BB} + x_A x_B (2E_{AB} - E_{AA} - E_{BB})). \quad (5.16)$$

If the reference states are taken as pure  $A$  and  $B$  then Eq. (5.16) reverts to

$$H_{\text{mix}} = \frac{Nz}{2} x_A x_B (2E_{AB} - E_{AA} - E_{BB}) \quad (5.17)$$

where  $H_{\text{mix}}$  is the enthalpy of mixing. If the bond energies are temperature dependent there will also be an excess entropy of mixing leading to the well-known regular solution model for the Gibbs excess energy of mixing

$$G_{\text{mix}}^{xs} = x_A x_B \Omega \quad (5.18)$$

where  $\Omega$  is now a temperature-dependent interaction parameter. When generalised and added to Eq. (5.13) this gives

$$G_m = \sum_i x_i G_i^0 + RT \sum_i x_i \log_e x_i + \sum_i \sum_{j>i} x_i x_j \Omega_{ij} \quad (5.19)$$

However, it has been realised for a long time that the assumption of composition-independent interactions was too simplistic. This led to the development of the sub-regular solution model, where interaction energies are considered to change linearly with composition. The following expression for  $G_{\text{mix}}^{xs}$  is then obtained as (Kaufman and Bernstein 1970)

$$G_{\text{mix}}^{xs} = x_i x_j (\Omega_{ij}^i x_i + \Omega_{ij}^j x_j) \quad (5.20)$$

Taking this process further, more complex composition dependencies to  $\Omega$  can be considered and it is straightforward to show that a general formula in terms of a power series should provide the capability to account for most types of composition dependence (Tomiska 1980). The most common method is based on the Redlich-Kister equation and Eq. (5.19) is expanded to become

$$G_m = \sum_i x_i G_i^0 + RT \sum_i x_i \log_e x_i + \sum_i \sum_{j>i} x_i x_j \sum_v \Omega_{ij}^v (x_i - x_j)^v \quad (5.21)$$

where  $\Omega_{ij}^v$  is a binary interaction parameter dependent on the value of  $v$ . The above equation for  $G_{\text{mix}}^{xs}$  becomes regular when  $v = 0$  and sub-regular when  $v = 1$ . In practice the value for  $v$  does not usually rise above 2. If it is found necessary to do so, it is probable that an incorrect model has been chosen to represent the phase.

Equation (5.21) assumes ternary interactions are small in comparison to those which arise from the binary terms. This may not always be the case and where evidence for higher-order interactions is evident these can be taken into account by a further term of the type  $G_{ijk} = x_i x_j x_k L_{ijk}$ , where  $L_{ijk}$  is an excess ternary interaction parameter. There is little evidence for the need for interaction terms of any higher order than this and prediction of the thermodynamic properties of substitutional solution phases in multi-component alloys is usually based on an assessment of binary and ternary terms. Various other polynomial expressions for the excess term have been considered, see for example the reviews by Ansara (1979) and Hillert (1980). All are, however, based on predicting the properties of

References are listed on pp. 124-126.

the higher-order system from the properties of the lower-component systems.

Equation (5.21) is normally used in metallic systems for substitutional phases such as liquid, b.c.c., f.c.c., etc. It can also be used to a limited extent for ceramic systems and useful predictions can be found in the case of quasi-binary and quasi-ternary oxide systems (Kaufman and Nesor 1978). However, for phases such as interstitial solutions, ordered intermetallics, ceramic compounds, slags, ionic liquids and aqueous solutions, simple substitutional models are generally not adequate and more appropriate models will be discussed in Sections 5.4 and 5.5.

**5.3.1.4 The extrapolation of the Gibbs excess energy to multi-component systems.** As mentioned in the previous section, most methods of extrapolating the thermodynamic properties of alloys into multi-component systems are based on the summation of the binary and ternary excess parameters. The formulae for doing this are based on various geometrical weightings of the mole fractions (Hillert 1980). To demonstrate this principle, emphasis will be given to three of the main methods which have been proposed. For simplicity the binary systems will be represented as sub-regular solutions.

*Muggianu's equation*

The predominant method at the present time uses the equation developed by Muggianu *et al.* (1975). In this circumstance the excess energy in a multi-component system, as given by the last term of Eq. (5.21), expands for a sub-regular solution to

$$G_{\text{mix}}^{xs} = x_A x_B \{L_{AB}^0 + L_{AB}^1(x_A - x_B)\} + x_B x_C \{L_{BC}^0 + L_{BC}^1(x_B - x_C)\} + x_A x_C \{L_{AC}^0 + L_{AC}^1(x_A - x_C)\} \quad (5.22)$$

*Kohler's equation*

In the Kohler equation (Kohler 1960)  $G_{\text{mix}}^{xs}$  is described by

$$G_{\text{mix}}^{xs} = (x_A + x_B)^2 \frac{x_A}{x_A + x_B} \cdot \frac{x_B}{x_A + x_B} \left\{ L_{AB}^0 + L_{AB}^1 \left( \frac{x_A - x_B}{x_A + x_B} \right) \right\} + (x_B + x_C)^2 \frac{x_B}{x_B + x_C} \cdot \frac{x_C}{x_B + x_C} \left\{ L_{BC}^0 + L_{BC}^1 \left( \frac{x_B - x_C}{x_B + x_C} \right) \right\} + (x_A + x_C)^2 \frac{x_A}{x_A + x_C} \cdot \frac{x_C}{x_A + x_C} \left\{ L_{AC}^0 + L_{AC}^1 \left( \frac{x_A - x_C}{x_A + x_C} \right) \right\} \quad (5.23)$$

Although different in form to the Muggianu equation, it becomes identical in a binary system as the various terms ( $x_i + x_j$ ) terms become equal to 1.

may be preferable. In practice, the phase boundaries calculated by either the Muggianu and Kohler extrapolations seem to provide comparable results (Ansara *et al.* 1978), but it was noted that the choice of extrapolation method should receive more attention when exact knowledge of partial quantities such as activity coefficients is more critical. The Toop equation is not suitable for metallic systems but may be appropriate for some ionic liquid systems. However, it should be used with care in all cases as the extrapolation is dependent on which binary is chosen to behave differently, and it is possible to obtain three different answers depending on this choice.

#### 5.4. SUBLATTICE MODELS

##### 5.4.1 Introduction

A *sublattice phase* can be envisaged as being composed of interlocking sublattices (Fig. 5.3) on which the various components can mix. It is usually crystalline in nature but the model can also be extended to consider ionic liquids where mixing on particular 'ionic sublattices' is considered. The model is phenomenological in nature and does not define any crystal structure within its general mathematical formulation. It is possible to define internal parameter relationships which reflect structure with respect to different crystal types, but such conditions must be externally formulated and imposed on the model. Equally special relationships apply if the model is to be used to simulate order-disorder transformations.

Sublattice modelling is now one of the most predominant methods used to describe solution and compound phases. It is flexible and can account for a variety of different phase types ranging from interstitial phases such as austenite and ferrite in steels to intermetallic phases, such as sigma and Laves, which have wide homogeneity ranges. Furthermore, it can be extended to simulate Bragg-Williams-Gorsky ordering in metallic systems and be adapted to account for

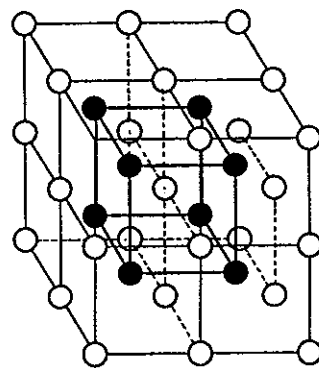


Figure 5.3. Simple body-centred cubic structure with preferential occupation of atoms in the body-centre and corner positions.

#### Toop's equation

Both the Muggianu and Kohler equations can be considered symmetrical as they treat the components in the same way and do not differentiate between them. This is true for another method suggested by Colinet (1967) which is derived differently than either the Kohler or Muggianu equations but which can be reduced to the Muggianu equation (Hillert 1980). Toop's equation (1965) is essentially different in that it considers one of the binary systems does not behave in the same way as the others and the extrapolation is based essentially on two of the binaries having identical mole-fraction products with the mole-fraction products of the third being different. For a sub-regular solution Toop's equation breaks down to (Hillert 1980)

$$G_{\text{mix}}^{\text{rs}} = x_A x_B \left\{ L_{AB}^0 + L_{AB}^1 (x_A - x_B - x_C) \right\} + x_A x_C \left\{ L_{AC}^0 + L_{AC}^1 (x_A - x_C - x_B) \right\} + x_B x_C \left\{ L_{BC}^0 + L_{BC}^1 \left( x_B - x_C + \frac{x_B - x_C}{x_B + x_C} x_A \right) \right\} \quad (5.24)$$

Again this reduces to the normal sub-regular form in the binaries.

The geometrical representation of the Muggianu, Kohler and Toop equations is best summarised using the figures below.

In the Muggianu extrapolation it can be seen that the line from the ternary alloy composition to the edge binaries forms a right-angle to the binary. This has the consequence that, when the alloy composition is dilute in two of the components, the interaction parameter of these two components will approach regular behaviour because the term  $(x_i - x_j)$  becomes small. This is the case even if the ratio  $x_i : x_j$  differs substantially from unity. This is not important for systems where the interaction terms higher than sub-regular are small in comparison to the regular term. However, for systems such as Cr-Ni where the sub-regular part predominates, any composition dependence of Cr-Ni interactions in dilute solutions with other elements will be ignored. This could have significant consequences in the prediction of activity coefficients in low-alloy steels for example. Kohler's equation allows for the composition dependence of the binaries and in these circumstances

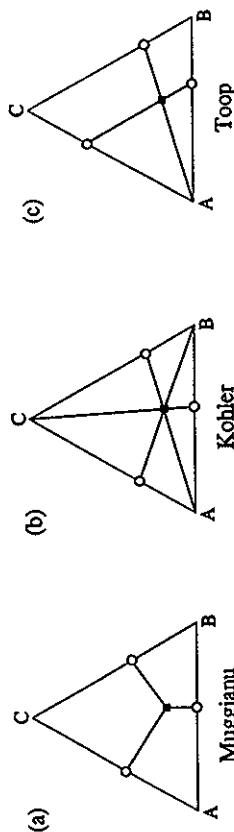


Figure 5.2. Geometrical constructions of (a) Muggianu, (b) Kohler and (c) Toop models.

ionic liquids. This section will begin by giving a detailed description of the multiple sublattice model of Sundman and Agren (1981) and give some specific examples of usage.

#### 5.4.2 The generalised multiple sublattice model (Sundman and Agren 1981)

**5.4.2.1 Definition of site fractions.** The multiple sublattice model is an extension of earlier treatments of the two-sublattice models of Hillert and Steffansson (1970), Harvig (1971) and Hillert and Waldenstrom (1977). It allows for the use of many sublattices and concentration dependent interaction terms on these sublattices. To work with sublattice models it is first necessary to define what are known as site fractions,  $y_i^s$ . These are basically the fractional site occupation of each of the components on the various sublattices where

$$y_i^s = \frac{n_i^s}{N^s} \quad (5.25)$$

$n_i^s$  is the number of atoms of component  $i$  on sublattice  $s$  and  $N^s$  is total number of sites on the sublattice. This can be generalised to include vacancies, which are important to consider in interstitial phases, such that Eq. (5.25) becomes

$$y_i^s = \frac{n_i^s}{n_{V_a}^s + \sum_i n_i^s} \quad (5.26)$$

and  $n_{V_a}^s$  is the number of vacancies on sublattice  $s$ . Mole fractions are directly related to site fractions by the following relationship

$$x_i = \frac{\sum_s N^s y_i^s}{\sum_s N^s (1 - y_{V_a}^s)} \quad (5.27)$$

**5.4.2.2 Ideal entropy of mixing.** The ideal entropy of mixing is made up of the configurational contributions by components mixing on each of the sublattices. The number of permutations which are possible, assuming ideal interchanges within each sublattice, is given by the following equation

$$W_P = \prod_s \frac{N^s!}{n_i^s!} \quad (5.28)$$

and the molar Gibbs ideal mixing energy is

References are listed on pp. 124–126.

$$G_{\text{mix}}^{\text{ideal}} = -TS_{\text{mix}}^{\text{ideal}} = RT \sum_s N^s \sum_i y_i^s \log_e y_i^s \quad (5.29)$$

where  $y_i^s$  includes contribution from vacancies.

**5.4.2.3 Gibbs energy reference state.** The Gibbs energy reference state is effectively defined by the 'end members' generated when only the pure components exist on the sublattice. Envisage a sublattice phase with the following formula  $(A, B)_1(C, D)_1$ . It is possible for four points of 'complete occupation' to exist where pure  $A$  exists on sublattice 1 and either pure  $B$  or  $C$  on sublattice 2 or conversely pure  $B$  exists on sublattice 1 with either pure  $B$  or  $C$  on sublattice 2. The composition space of the phase can then be considered in Fig. 5.4 below as consisting of four compounds, the so-called 'end members', at the corner of each square. The composition of the phase is then encompassed in the space between the four 'end member' compounds (Fig. 5.4(a)) and the reference energy surface will look like Fig. 5.4(b).

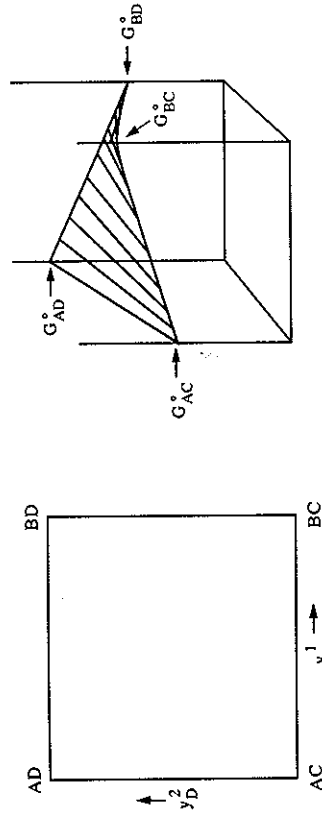


Figure 5.4. (a) Composition space encompassed by the system  $(A, B)_1(C, D)_1$  and (b) the reference energy surface described by equation (5.30) after Hillert and Stafansson (1980).

The surface in Fig. 5.4(b) can be represented by the equation

$$G_m^{\text{ref}} = y_A y_C G_{AC}^0 + y_B y_C G_{BC}^0 + y_A y_D G_{AD}^0 + y_B y_D G_{BD}^0 \quad (5.30)$$

Equation (5.30) holds for the simple case of a phase with the formula  $(A, B)_1(C, D)_1$ . But for more complex phases the function for the Gibbs reference energy surface may be generalised by arranging the site fractions in a  $(l + c)$  matrix if there are  $l$  sublattices and  $c$  components.

$$y = \begin{pmatrix} y_1^1 & y_2^1 & y_3^1 & \dots & y_c^1 \\ y_1^2 & y_2^2 & y_3^2 & \dots & y_c^2 \\ y_1^3 & y_2^3 & y_3^3 & \dots & y_c^3 \\ \dots & \dots & \dots & \dots & \dots \\ y_1^l & y_2^l & y_3^l & \dots & y_c^l \end{pmatrix}$$

Each row represents a sublattice and each column a component. The information contained in the subscript and superscript can be represented by a component array  $I$ , which defines one component for each sublattice. Using this notation a more generalised formula can be obtained (Sundman and Ågren 1981)

$$G_m^{\text{ref}} = \sum_I P_I(Y) \cdot G_I^{\text{ref}} \quad (5.31)$$

where  $G_I^{\text{ref}}$  represent the Gibbs energy of the compound defined by  $I$  and  $P_I(Y)$  represents the corresponding product of site fractions from the  $Y$  matrix.

**5.4.2.4 Gibbs excess energy of mixing.** The method for describing the Gibbs excess energy can, again, be best shown by using a two-sublattice system  $(A, B)_1(C, D)_1$  before generalising to a multi-component system. In this alloy  $A-C$ ,  $A-D$ ,  $B-C$  and  $B-D$  interactions are controlled by the Gibbs energy of the compounds  $AC$ ,  $BC$ ,  $AD$  and  $BD$ . Mixing on the sublattices controls  $A-B$  and  $C-D$  interactions and the simplest form of interaction is a regular solution format such that

$$G_{\text{mix}}^{\text{exs}} = y_A^1 y_B^1 L_{A,B}^0 + y_C^1 y_D^1 L_{C,D}^0 \quad (5.32)$$

where  $L_{A,B}^0$  and  $L_{C,D}^0$  denote regular solution parameters for mixing on the sublattices irrespective of site occupation of the other sublattice. A sub-regular model can be introduced by making the interactions compositionally dependent on the site occupation in the other sublattice.

$$G_{\text{mix}}^{\text{exs}} = y_A^1 y_B^1 y_C^2 L_{A,B,C}^0 + y_A^1 y_B^1 y_D^2 L_{A,B,D}^0 + y_C^1 y_D^1 y_A^2 L_{A,C,D}^0 + y_C^1 y_D^1 y_B^2 L_{B,C,D}^0 \quad (5.33)$$

Finally some site fraction dependence to these parameters can be added such that

$$L_{A,B,C}^0 = y_A^1 y_B^1 y_C^2 \sum_v L_{A,B,C}^v (y_A^1 - y_B^1)^v \quad (5.34a)$$

$$L_{A,B,D}^0 = y_A^1 y_B^1 y_D^2 \sum_v L_{A,B,D}^v (y_A^1 - y_B^1)^v \quad (5.34b)$$

$$L_{A,C,D}^0 = y_A^1 y_C^2 y_D^2 \sum_v L_{A,C,D}^v (y_C^2 - y_D^2)^v \quad (5.34c)$$

$$L_{B,C,D}^0 = y_B^1 y_C^2 y_D^2 \sum_v L_{B,C,D}^v (y_C^2 - y_D^2)^v \quad (5.34d)$$

It is clear that this can be expanded to any number of sublattices and components and Eq. (5.33) can be generalised using the notation of Eq. (5.31)

$$G_{\text{mix}}^{\text{exs}} = \sum_{\Pi} P_{\Pi}(Y) \cdot L_{\Pi} \quad (5.35)$$

$I_1$  refers to a component array of the first order, where one sublattice contains two components, but the remaining sublattices are occupied by only one component with the summation being taken over all different  $I_1$ . The type of component array that was introduced in Eq. (5.31) can then be denoted  $I_0$  and referred to as a component of the zeroth order. Equation (5.35) is general for the case of regular solutions but can be further extended to include interactions of a higher order, as in Eq. (5.34), by introducing the appropriate arrays  $I_2$  but with a further restriction that component array must not contain any component more than once in each sublattice. In this way the excess Gibbs energy can be written as

$$G_{\text{mix}}^{\text{exs}} = \sum_{Z>0} \sum_{I_2} P_{I_2}(Y) \cdot L_{I_2} \quad (5.36)$$

and the total energy of the phase including the reference energy, the ideal entropy and excess terms becomes

$$G_m^{\text{ref}} = \sum_{I_0} P_{I_0}(Y) \cdot G_{I_0}^{\text{ref}} + RT \sum_s N^s \sum_t y_t^s \log_e y_t^s + \sum_{Z>0} \sum_{I_2} P_{I_2}(Y) \cdot L_{I_2} \quad (5.37)$$

### 5.4.3 Applications of the sublattice model

**5.4.3.1 Line compounds.** These are phases where sublattice occupation is restricted by particular combinations of atomic size, electronegativity, etc., and there is a well-defined stoichiometry with respect to the components. Many examples occur in transition metal borides and silicides,  $III-V$  compounds and a number of carbides. Although such phases are considered to be stoichiometric in the relevant binary systems, they can have partial or complete solubility of other components with preferential substitution for one of the binary elements. This can be demonstrated for the case of a compound such as the orthorhombic  $\text{Cr}_2\text{B}$ -type boride which exists in a number of refractory metal-boride phase diagrams. Mixing then occurs by substitution on the metal sublattice.

For example in the  $\text{Fe-Cr-B}$  system (Fig. 5.5)  $\text{Cr}_2\text{B}$  extends across the diagram at a constant stoichiometry of boron as  $(\text{Cr,Fe})_2\text{B}$  (Villars and Calvert 1985). Also shown is the corresponding extension of the tetragonal  $\text{Fe}_2\text{B}$  compound. Such phases are commonly called 'line compounds'. Generally, sublattice occupation can be described as

$$(A, B, C \dots)_u(Z)_v$$

where  $A$ ,  $B$  and  $C$  are the elements which mix on the first sublattice and  $Z$  is the element with fixed stoichiometry. The Gibbs energy of such a phase can be written

$$G_m = \sum_t y_t^1 G_{i,t}^{\text{ref}} + RT u \sum_t y_t^1 \log_e y_t^1 + \sum_t \sum_{j>t} y_t^1 y_j^1 \sum_v L_{ij}^v (y_t^1 - y_j^1)^v \quad (5.38)$$

$$\begin{aligned}
 G_m = & y_{Cr}^1 y_{Va}^2 G_{Cr:Va}^0 + y_{Fe}^1 y_{Va}^2 G_{Fe:Va}^0 + y_{Cr}^1 y_{Cr:C}^2 G_{Cr:C}^0 \\
 & + y_{Fe}^1 y_{Cr:C}^2 G_{Fe:C}^0 + RT \left( 1 \cdot (y_{Cr}^1 \log_e y_{Cr}^1 + y_{Fe}^1 \log_e y_{Fe}^1) \right. \\
 & + 1 \cdot (y_{Cr}^2 \log_e y_{Cr}^2 + y_{Va}^2 \log_e y_{Va}^2) \\
 & + y_{Cr}^1 y_{Fe}^1 y_{Va}^2 \left( \sum_v L_{Cr:Fe:Va}^v (y_{Cr}^1 - y_{Fe}^1)^v \right) \\
 & + y_{Cr}^1 y_{Fe}^1 y_{Cr:C}^2 \left( \sum_v L_{Cr:Fe:C}^v (y_{Cr}^1 - y_{Fe}^1)^v \right) \\
 & + y_{Cr}^1 y_{Cr:C}^2 y_{Va}^2 \left( \sum_v L_{Cr:C:Va}^v (y_{Cr}^1 - y_{Va}^2)^v \right) \\
 & + y_{Fe}^1 y_{Cr:C}^2 y_{Va}^2 \left( \sum_v L_{Fe:C:Va}^v (y_{Cr}^1 - y_{Va}^2)^v \right).
 \end{aligned}
 \tag{5.39}$$

The first two terms represent the Gibbs energy of f.c.c.\_A1 Cr and Fe because the second sublattice consists entirely of unfilled interstitial sites. The next two terms represent the Gibbs energy of the CrC and FeC compounds which are formed when all of the interstitial sites of the f.c.c.\_A1 lattice are filled with C. The second line is the ideal entropy term while the last four lines correspond to the excess term. It can be seen that, when  $y_C^2 = 0$ , the model reduces to Eq. (5.21) for the simple substitutional mixing of Cr and Fe. This is particularly useful as thermodynamic assessments of metallic binary systems can be extended to include interstitial elements without the need for changing any of the existing parameters.

**5.4.3.3 Complex intermetallic compounds with significant variation in stoichiometry.** In many binary systems intermetallic compounds may exhibit significant solubility and there may be more than two crystallographic sublattices to consider. This is the case for compounds such as the  $\sigma$ ,  $\mu$ ,  $\chi$  and Laves phases, and in such circumstances the sublattice model should, as closely as possible, follow the internal sublattice structure of the compound itself. Taking the case of  $\sigma$ , this consists of five crystallographically distinct sublattices occupied by atoms in the ratio 2:4:8:8:8 (Villars and Calvert 1991). The total number of atoms per unit cell is then 30. Full mixing of all components on all sublattices yields a prohibitively high number of variables, making a CALPHAD calculation in a multi-component system almost impossible. Even modelling the phase in a binary would be extremely difficult and some simplification is necessary.

This can be achieved for  $\sigma$  by considering two types of components differentiated almost exclusively by size considerations. The sublattice occupation can then be simplified. One possibility is to consider  $\sigma$  as either  $(A, B)_{16}(A, B)_{10}(B)_4$  where the first and third sublattices and fourth and fifth sublattices are 'joined', i.e., site occupation of A and B atoms are considered to be equal on the sites. Alternatively  $(A, B)_{16}(A)_{10}(B)_4$  may be used where mixing is considered only to occur on the

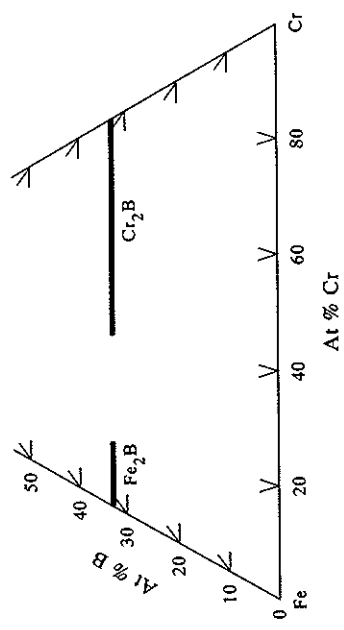
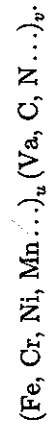


Figure 5.5. Partial isothermal section for Fe-Cr-B showing stoichiometric behaviour of the  $(Cr,Fe)_2B$  compound.

where  $i$  and  $j$  denote the elements mixing on sublattice 1 while Z is the stoichiometric element.  $u$  is the molar number of sites in sublattice 1 and  $G_{i,z}^0$  denotes the Gibbs energies of the various compounds when sublattice 1 is completely occupied by one of the components mixing on sublattice 1. The excess energy term is associated only with interactions between the components on the first sublattice. Because of the fixed stoichiometry, mole fractions can straightforwardly be expressed as  $x_i = (u/(u+v)) y_i^1$  and Eq. (5.38) becomes equivalent to the line compound models used by Kaufman and Bernstein (1970).

**5.4.3.2 Interstitial phases.** These are predominant in steels and ferrous-based alloys, where elements such as C and N occupy the interstitial sites of the ferrite and austenite lattices. In this case the structure of the phase can be considered as consisting of two sublattices, one occupied by substitutional elements, such as Fe, Cr, Ni, Mn, etc., and the other occupied by the interstitial elements, such as C or N, and interstitial vacancies (Va). As the concentration of C, N, ..., etc., increases the interstitial vacancies are filled until there is complete occupation. The occupation of the sublattices is shown below as



In the case of an f.c.c.\_A1 structure, with  $u = v = 1$ , the state of complete occupation of interstitial carbon corresponds to a MC carbide with the NaCl lattice. For the c.p.h.\_A3 structure, with  $u = 1$  and  $v = 0.5$ , complete occupation of the interstitial sites by carbon gives the  $M_2C$  carbide with a hexagonal  $Fe_2N$ -type structure.

For the case of the f.c.c.\_A1, austenite phase in Cr-Fe-C, the Gibbs energy of the phase is represented by the formula  $(Cr, Fe)_1(C, Va)_1$  and its Gibbs energy given by the following equation

References are listed on pp. 124-126.



fourth and fifth sublattices (Ansara *et al.* 1997). The latter occupation arises when solubility of *B* components is small in the second sublattice, as appears to be the case for most  $\sigma$  phases. The consequence of this simplification is that the sublattice formula for the Co-Mo  $\sigma$  phase is given by  $(\text{Co}, \text{Mo})_{16}(\text{Co})_{10}(\text{Mo})_4$  and the Gibbs energy is then

$$G_m = G_{\text{Co}_0\text{Co}_0\text{Mo}_0}^0 + G_{\text{Mo}_0\text{Co}_0\text{Mo}_0}^0 + RT \left( 16 \cdot (y_{\text{Co}_0}^1 \log_e y_{\text{Co}_0}^1 + y_{\text{Mo}_0}^1 \log_e y_{\text{Mo}_0}^1) \right. \\ \left. + y_{\text{Co}_0}^1 y_{\text{Mo}_0}^1 y_{\text{Co}_0}^2 y_{\text{Mo}_0}^2 \left( \sum_{\nu} L_{\text{Co}_0\text{Mo}_0\text{Co}_0\text{Mo}_0}^{\nu} (y_{\text{Co}_0}^1 - y_{\text{Mo}_0}^1)^{\nu} \right) \right) \quad (5.40)$$

As  $y_{\text{Co}_0}^2 = y_{\text{Mo}_0}^2 = 1$ , Eq. (5.40) becomes rather like Eq. (5.21) in that mixing is simplified to two components on a single sublattice but the points of complete occupation do not reach pure Co or Mo. The expressions for Gibbs energy become more complex when, with the addition of further elements, mixing can occur on all sublattices as in the case of Ni-Co-Mo-W. Here the sublattice formula would be  $(\text{Ni}, \text{Co}, \text{Mo}, \text{W})_{16}(\text{Ni}, \text{Co})_{10}(\text{Mo}, \text{W})_4$ , but this degree of complexity can be handled straightforwardly by most current software.

**5.4.3.4 Order-disorder transformations.** The previous examples considered strict site preference for the components in sublattice phases. For example, in the  $(\text{Cr}, \text{Fe})_2\text{B}$  compound, B is not considered to mix on the metal sublattice, nor are Cr and Fe considered to mix on the B sublattice. This strict limitation on occupancy does not always occur. Some phases, which have preferential site occupation of elements on different sublattices at low temperatures, can disorder at higher temperatures with all elements mixing randomly on all sublattices.

It was demonstrated by Sundman (1985) and later by Ansara *et al.* (1988) that an order-disorder transformation could be modelled by setting specific restrictions on the parameters of a two-sublattice phase. One of the first phases to be considered was an  $A_3B$ -ordered compound. In such circumstances the sublattice formula  $(A, B)_3(A, B)$  can be applied and the possible relationships between site fractions and mole fractions are given in Figure 5.6. The dashed lines denoted  $x_B = 0.25$ , 0.5 and 0.75 show variations in order of the phase while the composition is maintained constant. When these lines cross the diagonal joining  $A_3A$  and  $B_3B$  the phase has disordered completely as  $y_B^2 = y_B^1 = x_B$ . As the lines go toward the boundary edge the phase orders and, at the side and corners of the composition square, there is complete ordering of *A* and *B* on the sublattices.

The *two-sublattice order-disorder model* (2SLOD) requires first that the Gibbs energy should always have an extremum along the diagonal representing the disordered state with respect to fluctuations in site fractions at constant composition. Further, when the disordered phase is stable this extremum must be a minimum. By assuming that  $G_{A:A}^0$  and  $G_{B:B}^0$  are zero and applying the above conditions it is possible to define interconnected parameters for the various values

References are listed on pp. 124-126.

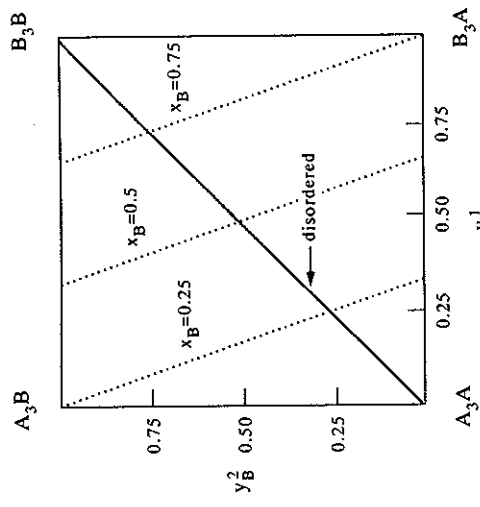


Figure 5.6. Relationship between site and atomic fractions in the 2SLOD model for  $\text{Ni}_3\text{Al}$ .

of  $G_{A:B}^0$  and  $G_{B:A}^0$  and the excess mixing terms, such that the  $A_3B$  phase is ordered at low temperature but disorders as the temperature is increased. For the case of an  $A_3B$  compound one solution gives (Ansara *et al.* 1988)

$$G_{A:B}^0 = u_1 \\ G_{B:A}^0 = u_2 \\ L_{A,B:A}^0 = 3u_1 + u_2/2 + 3u_3 \\ L_{A,B:B}^0 = u_1/2 + 3u_2 + 3u_3 \\ L_{A:A,B}^0 = u_2/2 + u_3 \\ L_{B,A,B}^0 = u_1/2 + u_3 \\ L_{A,B:A}^1 = 3u_4 \\ L_{A,B:B}^1 = 3u_5 \\ L_{A:A,B}^1 = u_4 \\ L_{B,A,B}^1 = u_5 \\ L_{A,B:A,B}^0 = 4u_4 - 4u_5 \quad (5.41)$$

The above terms give the ordering contribution to the total energy, and to provide the necessary disordered energy it was necessary to add further terms. This is done by using the relationships

$$x_A = u \cdot y_A^1 + v \cdot y_A^2 \quad \text{and} \quad x_B = u \cdot y_B^1 + v \cdot y_B^2 \quad (5.42)$$