

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 σ phases. The consequence of this simplification is that the sublattice formula for the Co–Mo σ phase is given by $(\text{Co}, \text{Mo})_{16}(\text{Co})_{10}(\text{Mo})_4$ and the Gibbs energy is then

$$G_m = G_{\text{Co:Co:Mo}}^0 + G_{\text{Mo:Co:Mo}}^0 + RT(16 \cdot (y_{\text{Co}}^1 \log_e y_{\text{Co}}^1 + y_{\text{Mo}}^1 \log_e y_{\text{Mo}}^1)) + y_{\text{Co}}^1 y_{\text{Mo}}^1 y_{\text{Co}}^2 y_{\text{Mo}}^3 \left(\sum_{\nu} L_{\text{Co}_1\text{Mo}_1\text{Co}_1\text{Mo}_1}^{\nu} (y_{\text{Co}}^1 - y_{\text{Mo}}^1)^{\nu} \right). \quad (5.40)$$

As $y_{\text{Co}}^2 = y_{\text{Mo}}^2 = 1$, 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 $y_B^1 = y_B^2 = x_B$. 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.

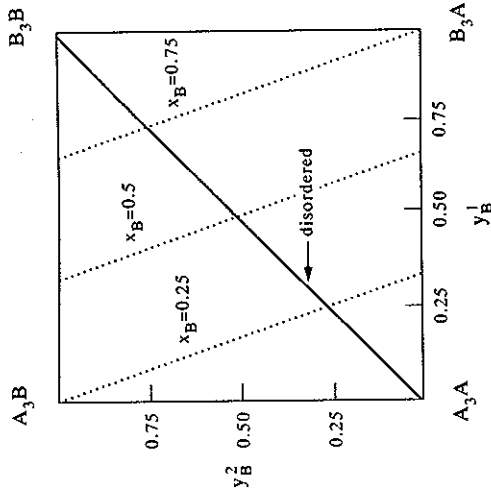


Figure 5.6. Relationship between site and atomic fractions in the 2SLOD model for Ni_3Al .

of $G_{A:A}^0$ 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)

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

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

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

where u and v are the number of sites on sublattices 1 and 2. Replacing x_A and x_B in Eq. (5.21), expanding and comparing with the formula for the two-sub-lattice model, an equivalence in Gibbs energy between the disordered substitutional solid solution and a two-sublattice model can be obtained if the following parameters are used (Saunders 1989):

$$\begin{aligned}
 G_{A,B}^0 &= w \cdot L_{AB}^0 + wv(u-v) \cdot L_{AB}^1 + wv(u-v)^2 \cdot L_{AB}^2 \\
 G_{B,A}^0 &= w \cdot L_{AB}^0 - wv(u-v) \cdot L_{AB}^1 + wv(u-v)^2 \cdot L_{AB}^2 \\
 L_{A,B:A}^0 &= u^2 \cdot L_{AB}^0 + 3u^2v \cdot L_{AB}^1 + u^2v(5v-2u) \cdot L_{AB}^2 \\
 L_{A,B:B}^0 &= u^2 \cdot L_{AB}^0 - 3u^2v \cdot L_{AB}^1 + v^2v(5v-2u) \cdot L_{AB}^2 \\
 L_{A,B:A}^1 &= u^3 \cdot L_{AB}^1 + 4u^3v \cdot L_{AB}^2 \\
 L_{A,B:B}^1 &= v^3 \cdot L_{AB}^1 - 4v^3v \cdot L_{AB}^2 \\
 L_{A,B:A}^2 &= u^4 \cdot L_{AB}^2 \\
 L_{A,B:B}^2 &= v^4 \cdot L_{AB}^2 \\
 L_{A:A,B}^0 &= v^2 \cdot L_{AB}^0 + 3v^2u \cdot L_{AB}^1 + v^2u(5u-2v) \cdot L_{AB}^2 \\
 L_{B:A,B}^0 &= v^2 \cdot L_{AB}^0 - 3v^2u \cdot L_{AB}^1 + v^2u(5u-2v) \cdot L_{AB}^2 \\
 L_{A:A,B}^1 &= v^3 \cdot L_{AB}^1 + 4v^3u \cdot L_{AB}^2 \\
 L_{B:A,B}^1 &= v^3 \cdot L_{AB}^1 - 4v^3u \cdot L_{AB}^2 \\
 L_{A:A,B}^2 &= v^4 \cdot L_{AB}^2 \\
 L_{B:A,B}^2 &= v^4 \cdot L_{AB}^2 \\
 L_{A,B:A,B}^0 &= -24u^2v^2 \cdot L_{AB}^2
 \end{aligned}
 \tag{5.43}$$

where $L_{AB}^{0,1,2}$ are the respective excess parameters from Eq. (5.21) (note L replaces Ω in the above notation). Adding the ordered and disordered part together provides the total Gibbs energy of the phase both in the ordered and disordered state. This method was used by Gros (1987), Ansara *et al.* (1988) and Saunders (1989) and, in general, calculations give quite reasonable results. However, the model proved to have some flaws (Saunders 1996). Firstly, when asymmetrical terms for the ordering energies are used (i.e., $v_1 \neq v_2$) they give rise to a residual, extraneous excess Gibbs energy when the phase disordered and there is no longer an equivalence in Gibbs energy between the 2SLOD model and the original disordered phase. Secondly, when the disordered part is extended to higher order systems there is an incompatibility with the substitutional model when sub-regular or higher terms are used for the various $L_{0,1,2}$ parameters in Eq. (5.43).

Some of the problems with the model were addressed in later work by Dupin

(1995) who used a more complex formulation for the ordering parameters. Firstly, the ordering contribution was separated from disordered contribution and added straightforwardly to the Redlich–Kister energy polynomial. This also made it simpler to combine with a Redlich–Kister model and removed the need for re-formatting existing phases already modelled using this format. Secondly, the extraneous excess energies from the ordering parameters were empirically removed such that the excess Gibbs energy due to the ordered parameters became zero on disordering. The Gibbs energy is then expressed as a sum of three terms

$$G_m = G_m^{\text{dis}}(x_i) + G_m^{\text{ord}}(y_i^1 y_i^2) - G_m^{\text{ord}}(y_i^1 = x_i; y_i^2 = x_i) \tag{5.44}$$

where $G_m^{\text{dis}}(x_i)$ is the Gibbs energy contribution of the disordered state, $G_m^{\text{ord}}(y_i^1 y_i^2)$ is the Gibbs energy contribution due to ordering and $G_m^{\text{ord}}(y_i^1 = x_i; y_i^2 = x_i)$ is a term which represents the extraneous excess energy contribution from the ordered parameters when the phase disorders. A more accurate representation of the Ni–Al diagram was achieved using this model (Dupin 1995) and the work was extended to Ni–Al–Ti–Cr and Ni–Al–Ta–Cr.

However, the empirical removal of the residual, extraneous energies, $G_m^{\text{ord}}(y_i^1 = x_i; y_i^2 = x_i)$, causes internal inconsistencies in the model. For example, in an ordered compound such as an AB or A_3B type, it is possible that the Gibbs energy which is *actually* calculated for the fully ordered state is quite different from that specified for G_{AB}^{ord} or $G_{A_3B}^{\text{ord}}$ (Saunders 1996). It would therefore be better if the model was derived in such a way that these extraneous energies did not arise. This is actually the case when ordering energies are symmetrical in the form where $G_{A,B}^0 = G_{B,A}^0$ and $L_{A,B}^0 = L_{B,A}^0 = -G_{A,B}^0$ (Saunders 1989). This is equivalent to the conditions of the Bragg–Williams–Gorsky model of Inden (1975a, 1975b, 1977a, 1977b). However, this limits the model when it is applied to phases such as Ti_3Al and Ni_3Al where substantial asymmetries are apparent.

The empirical nature of the 2SLOD model is such that it cannot be considered a true ordering model in its own right and is therefore included in this chapter rather than the more fundamental chapter on ordering (Chapter 7). However, Sundman and Mohri (1990), using a hybrid sublattice model, showed it was possible to model the Cu–Au system such that it closely matched the phase diagram achieved by a Monte-Carlo method (see Chapter 7). This was done by combining a four-sublattice model, with composition-independent interaction energies, and a gas cluster model for the short-range ordering which was modified to account for a restriction in the degrees of freedom in the solid state. The sublattice model was equivalent to a classical Bragg–Williams (1934) treatment at low temperatures and therefore remains a basic ordering treatment. To model complex ordering systems such as Ti–Al it is almost certainly necessary to include at least third nearest-neighbour interchange energies (Pettifor 1995).

5.5. IONIC LIQUID MODELS

Phase diagrams containing ionic liquids, such as slag systems and molten salts, can be complex and show apparently contradictory behaviour. For example the SiO_2 -CaO phase diagram shows liquid immiscibility as well as thermodynamically stable compounds. Immiscibility is usually associated with positive deviations from ideality and, at first sight, is not consistent with compound-forming systems which exhibit large negative deviations. Such features arise from a complex Gibbs energy change with composition and, although the Gibbs energy of mixing can be negative over the whole composition range, inflections in the mixing curve give rise to spinodal points with subsequent decomposition to two liquids (Taylor and Dinsdale 1990). The use of simple mixture models for ionic liquids has not been successful. They need large numbers of coefficients to mimic the sharp changes in enthalpy around critical compositions, and binary systems thus modelled tend to predict the behaviour of multi-component systems badly.

Many models have been proposed to account for the thermodynamic behaviour of ionic liquids and some important ones are listed below:

- (1) Cellular models
- (2) Modified quasicheical models
- (3) Sublattice models
- (4) Associated solution models

The above is not intended to be a definitive list but rather to indicate some of the more commonly used models at the present time. Other, more historical, models have been used extensively, for example the polymerisation models of Toop and Samis (1962) and Masson (1965), the models of Flood (1954), Richardson (1956) and Yokakawa and Niwa (1969). More recently the 'central atom' model by Satsri and Lahiri (1985, 1986) and the 'complex' model of Hoch and Arpshofen (1984) have been proposed. Each has been used with some success in lower-order systems, but the extension to multicomponent systems is not always straightforward.

5.5.1 The cellular model

Kapoor and Froberg (1973) applied this model to the ternary system CaO-FeO-SiO₂. They envisaged that mixing occurred by formation of three 'asymmetric cells' obtained by a reaction between 'symmetric cells' of the metallic oxides and silica. For CaO-SiO₂, the formation energy for the asymmetric cell is denoted W_{IS} , where the subscripts I and S denote the combination of 'symmetric' cells from CaO and SiO₂. In addition interactions between the various symmetric and asymmetric cells were considered such that

$$\epsilon_{II,SS} = 2\epsilon_{IS,SS} \quad (5.45)$$

References are listed on pp. 124-126.

where $\epsilon_{II,SS}$ denotes the interaction between the symmetric CaO and SiO₂ cells and $\epsilon_{IS,SS}$ the interaction between the asymmetric cell formed between CaO and SiO₂ and the symmetric silica cell. This is expanded with the addition of FeO so that the two further asymmetric cells are formed with energies W_{JS} and W_{IJ} , where J denotes the FeO cell, and the additional interaction energies between the cells were related in the following way:

$$\epsilon_{IJ,SS} = \epsilon_{IS,SS} + \epsilon_{JS,SS} \quad (5.45a)$$

where $\epsilon_{JS,SS}$ is the interaction energy between the asymmetric cell formed between FeO and SiO₂ and the silica cell. It was further assumed that interactions terms were negligibly small in comparison to the cell formation energies and that $\epsilon_{IS,SS}/kT$ and $\epsilon_{JS,SS}/kT$ were small compared to unity. Based on these assumptions they were able to define the Gibbs energy of mixing in a system such as CaO-FeO-SiO₂ as

$$\begin{aligned} \frac{G_{\text{mix}}}{RT} = & -\frac{3N_S}{2} \log_e N_S - \frac{(1-N_S)}{2} \log_e(1-N_S) - N_I \log_e N_I - N_J \log_e N_J \\ & + (N_I - R_{IS} - R_{IJ}) \log_e(N_I - R_{IS} - R_{IJ}) \\ & + (N_J - R_{JS} - R_{IJ}) \log_e(N_J - R_{JS} - R_{IJ}) \\ & + (N_S - R_{IS} - R_{JS}) \log_e(N_S - R_{IS} - R_{JS}) \\ & + 2R_{IS} \log_e R_{IS} + 2R_{JS} \log_e R_{JS} + 2R_{IJ} \log_e R_{IJ} \\ & + \frac{2W_{IS}R_{IS}}{RT} + \frac{2W_{JS}R_{JS}}{RT} + \frac{2W_{IJ}R_{IJ}}{RT} \\ & + \frac{2\epsilon(1-N_S)(N_S - R_{IS} - R_{JS})}{RT} \end{aligned} \quad (5.46)$$

with

$$N_i = \sum_j \frac{n_i}{n_i + 2n_s}$$

and

$$N_S = \sum_i \frac{n_s}{n_i + 2n_s}$$

where i denotes either CaO or FeO and n_i and n_s denote the number of moles of CaO, FeO and SiO₂. The interaction parameter ϵ is given by

$$\epsilon = \frac{\sum_i n_i \epsilon_{IS,SS}}{\sum_i n_i}$$

and the various values of R_{ij} s by

$$R_{ij} = \frac{\tau_{ij}}{\sum_i n_i + 2n_s} \quad (5.48a)$$

$$(N_I - R_{IS} - R_{IT})(N_J - R_{JS} - R_{JT}) = R_{IJ}^2 \exp\left(-\frac{2W_{IJ}}{RT}\right) \quad (5.48b)$$

$$(N_I - R_{IS} - R_{IT})(N_S - R_{IS} - R_{JS}) = R_{IS}^2 \exp\left(-\frac{2W_{IS}}{RT}\right) \exp\left(-\frac{2e(1 - N_S)}{RT}\right) \quad (5.48c)$$

$$(N_J - R_{JS} - R_{JT})(N_S - R_{JS} - R_{JS}) = R_{JS}^2 \exp\left(-\frac{2W_{JS}}{RT}\right) \exp\left(-\frac{2e(1 - N_S)}{RT}\right) \quad (5.48d)$$

where τ_{ij} are the number of moles of the different asymmetric cell types. In Eq. (5.46) it can be seen that the first five lines correspond to the configurational entropy term. This is no longer ideal because of preferential formation of the various asymmetrical cells and the system effectively orders. This is a feature of ionic systems and gives rise to forms of quasi-chemical entropy which will also be discussed in the next section.

From the above equations, activities of metallic oxides and silica were calculated for various binary slag systems and CaO-FeO-SiO₂ and found to be in good agreement. The drawback of the model is that equivalents need to be made between various anionic and cationic types and problems can arise when these are polyvalent. Also, considering that only a ternary system was considered, the expressions for Gibbs energy are complex in comparison to the simple mixture and sublattice types. Gaye and Welfringer (1984) extended this model to multi-component systems but the treatment is too lengthy to consider here.

5.5.2 Modified quasi-chemical models

A modified form of the quasi-chemical model of Guggenheim (1935) and Fowler and Guggenheim (1939) has recently been developed by Pelton and Blander (1986a, 1986b, 1988) for application to ionic liquids. The model considers that the liquid has a strong tendency to order around specific compositions, associated with specific physical or chemical phenomena. This was considered to be a general feature of ionic liquids and that previous attempts at modelling of ordered salts and silicate slags were either too specific in nature to the type of system, i.e., oxide or

References are listed on pp. 124-126.

halide, or too complicated for general usage, particularly when considering extrapolation to higher-order systems. The model is therefore phenomenological in nature which has the advantage that it can be widely applied.

First, consider a binary liquid A-B in which A and B atoms mix substitutionally on a quasi-lattice with coordination number Z. There is the possibility that A-B pairs will be formed from A-A and B-B pairs by the following relation

$$(A-A) + (B-B) = 2(A-B).$$

The molar enthalpy and entropy change of this reaction, denoted respectively ω and η by Pelton and Blander (1986a, 1986b, 1988), is given by $(\omega - \eta T)$. If this is zero the solution is ideal. However, if $(\omega - \eta T)$ is negative then there will be ordering of the mixture around the 50:50 composition and the enthalpy and entropy of mixing will show distinct minima at the AB composition. As ordering does not always occur at AB it is desirable to allow other compositions to be chosen for the position of the minima, which is done by replacing mole fractions with equivalent fractions y_A and y_B where

$$y_A = \frac{\beta_A x_A}{\beta_A x_A + \beta_B x_B} \quad \text{and} \quad y_B = \frac{\beta_B x_B}{\beta_A x_A + \beta_B x_B} \quad (5.49)$$

where β_A and β_B are numbers chosen so that $y_A = y_B = 0.5$ at the composition of maximum ordering. Letting x_{AA} , x_{BB} and x_{AB} be the fractions of each type of pair in the liquid gives

$$H_{\text{mix}} = (\beta_A x_A + \beta_B x_B) \left(\frac{x_{AB}}{2}\right) \omega \quad (5.50)$$

$$S_{\text{mix}}^{\text{conf}} = -\frac{RZ}{2} (\beta_A x_A + \beta_B x_B) \cdot \left(x_{AA} \log_e \frac{x_{AA}}{y_A^2} + x_{BB} \log_e \frac{x_{BB}}{y_B^2} + x_{AB} \log_e \frac{x_{AB}}{2y_A y_B} \right) - R(x_A \log_e x_A + x_B \log_e x_B) \quad (5.51)$$

and

$$S_{\text{mix}}^{\text{exs}} = (\beta_A x_A + \beta_B x_B) \left(\frac{x_{AB}}{2}\right) \eta \quad (5.52)$$

where Z is the average co-ordination number. Two mass balance equations can be written

$$2y_A = 2x_{AA} + x_{AB} \quad (5.53a)$$

$$2y_B = 2x_{BB} + x_{AB} \quad (5.53b)$$

and minimisation of the Gibbs energy then gives the 'quasi-chemical equilibrium constant'

$$\frac{x_{AB}^2}{x_{AA}x_{BB}} = 4 \exp\left(\frac{-2(\omega - \eta T)}{zRT}\right) \tag{5.54}$$

Eqs (5.53) and (5.54) can be solved for any given values of ω and η to provide x_{AA} , x_{BB} and x_{AB} which can then be used to define the enthalpy and entropy values given in Eqs (5.50)–(5.52). The choice of β_A and β_B can be found using the following equation

$$(1 - r) \log_e(1 - r) + r \log_e r = 2\beta_B r \log_e 0.5 \tag{5.55}$$

where $r = \beta_A / (\beta_A + \beta_B)$. Finally, some simple compositional dependence is defined for ω and η

$$\omega = \sum_{n=0}^{\infty} \omega^n y_B^n \tag{5.56a}$$

and

$$\eta = \sum_{n=0}^{\infty} \eta^n y_B^n. \tag{5.56b}$$

The approach has been used effectively for a variety of systems, for example oxide and silicate slags, salt systems, and is readily extendable to multi-component systems (Pelton and Blander 1984, 1986a, 1986b, Blander and Pelton 1984). The general applicability of the model is demonstrated by the recent work of Eriksson *et al.* (1993) who are in the process of creating a comprehensive database for the system $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO--MnO--FeO--Na}_2\text{O--K}_2\text{O--TiO}_2\text{--Ti}_2\text{O}_3\text{--ZrO}_2\text{--S}$.

5.5.3 Sublattice models

Essentially, sublattice models originate from the concepts of Temkin (1945) who proposed that two separate sublattices exist in a solid-state crystal for cations and anions. The configurational entropy is then governed by the site occupation of the various cations and anions on their respective sublattices. When the valence of the cations and anions on the sublattices are equal, and electroneutrality is maintained, the model parameters can be represented as described in Section 5.4.2. However, when the valence of the cations and anions varies, the situation becomes more complex and some additional restrictions need to be made. These can be expressed by considering equivalent fractions (f) which, for a sublattice phase with the formula $(I^{+i}, J^{+j} \dots)(M^{-m}, N^{-n} \dots)$, are given by

$$f_I = \frac{iy_I^i}{\sum_I iy_I^i} \tag{5.57a}$$

and

References are listed on pp. 124–126.

$$f_M = \frac{my_M^m}{\sum_M my_M^m} \tag{5.57b}$$

where i and m are the valences of I and M respectively. These replace site fractions in the general expressions for the Gibbs energy reference and excess mixing terms. The ideal mixing term is given as (Pelton 1988)

$$\frac{G_{\text{mix}}^{\text{ideal}}}{RT} = \left(\sum_I iy_I^i\right) \left(\sum_I y_I^i \log_e y_I^i\right) + \left(\sum_M my_M^m\right) \left(\sum_M y_M^m \log_e y_M^m\right). \tag{5.58}$$

This approach works well for systems where no neutral ions exist and a database for the system (Li, Na, K)(F, Cl, OH, CO₃, SO₄) has been developed (Pelton 1988) which gives good estimates for activities in multi-component liquids. However, the above approach is more limited in the presence of neutral ions which are necessary if one wishes to model ionic liquids which may contain neutrals such as S.

To overcome this problem an extension of the sublattice model was proposed by Hillert *et al.* (1985) which is now known as the ionic two-sublattice model for liquids. As in the previous case it uses constituent fractions as composition variables, but it also considers that vacancies, with a charge corresponding to the charge of the cations, can be introduced on the anion sublattice so that the composition can move away from the ideal stoichiometry and approach an element with an electro-positive character. The necessary neutral species of an electronegative element are added to the anion sublattice in order to allow the composition to approach a pure element. The sublattice formula for the model can then be written as

$$(C_i^{+v_i})_P (A_j^{-v_j}, V_a, B_k^0)_Q \tag{5.59}$$

where C represents cations, A anions, V_a hypothetical vacancies and B neutrals. The charge of an ion is denoted v_i and the indices i, j and k are used to denote specific constituents. For the following description of the model, superscripts v_i, v_j and 0 will be excluded unless needed for clarity. The number of sites on the sublattices is varied so that electroneutrality is maintained and values of P and Q are calculated from the equation

$$P = \sum_j v_j y_{A_j} + Q y_{V_a} \tag{5.60a}$$

and

$$Q = \sum_I v_i y_{C_i} \tag{5.60b}$$

Eqs (5.60a) and (5.60b) simply mean that P and Q are equal to the average charge on the opposite sublattice with the hypothetical vacancies having an induced charge equal to Q . Mole fractions for the components can be defined as follows:

$$\text{Cations} \quad x_{C_i} = \frac{P y_{C_i}}{P + Q(1 - y_{V_a})} \quad (5.61a)$$

$$\text{Anions} \quad x_{D_i} = \frac{Q y_{D_i}}{P + Q(1 - y_{V_a})} \quad (5.61b)$$

The integral Gibbs energy for this model is then given by

$$\begin{aligned} G_m = & \sum_i y_{C_i} G_{C_i:A_j}^0 + Q y_{V_a} \sum_i y_{C_i} G_{C_i}^0 + Q \sum_k y_{B_k} G_{B_k}^0 \\ & + RT \left(P \sum_i y_{C_i} \log_e y_{C_i} + Q \left(\sum_j y_{A_j} \log_e y_{A_j} + y_{V_a} \log_e y_{V_a} \right. \right. \\ & \quad \left. \left. + \sum_k y_{B_k} \log_e y_{B_k} \right) \right) \\ & + \sum_{i_1 i_2} y_{i_1} y_{i_2} y_j L_{i_1 i_2:j} + \sum_{i_1 i_2} y_{i_1} y_{i_2} y_{V_a}^2 L_{i_1 i_2:V_a} \\ & + \sum_i y_{i_1} y_{j_1} y_{j_2} L_{i_1:j_1 j_2} + \sum_i y_i y_j y_{V_a} L_{i:j V_a} \\ & + \sum_i y_j y_k L_{i:j k} + \sum_i y_i y_k y_{V_a} L_{i:V_a k} \\ & + \sum_{k_1 k_2} y_{k_1} y_{k_2} L_{k_1 k_2} \end{aligned} \quad (5.62)$$

where $G_{C_i:A_j}^0$ is the Gibbs energy of formation for $(v_1 + v_2)$ moles of atoms of liquid $C_i A_j$ and $\Delta G_{C_i}^0$ and $\Delta G_{B_k}^0$ are the Gibbs energy of formation per mole of atoms of liquid C_i and B_k respectively. The first line represents the Gibbs energy reference state, the second line the configurational mixing term and the last three lines the excess Gibbs energy of mixing. As the list of excess parameters is long and the subscript notation is complex, it is worth giving some specific examples for these parameters after Sundman (1996):

$L_{i_1 i_2:j}$ represents the interaction between two cations in the presence of a common anion; for example $L_{Ca^{+2}Mg^{+2}O^{2-}}$ represents an interaction term from the system CaO-MgO.

$L_{i_1 i_2:V_a}$ represents interactions between metallic elements; for example $L_{Ca,Mg}$ in Ca-Mg.

References are listed on pp. 124-126.

$L_{i_1 i_2:j}$ represents interactions between two anions in the presence of a common cation; for example $L_{Ca^{+2}OH^{-1}CO_3^{2-}}$ in $Ca(OH)_2$ - $CaCO_3$.

$L_{i_1 i_2:j k}$ represents interactions between an anion and a neutral atom; for example $L_{Fe^{+2}S^{2-}S}$ in the S-rich part of Fe-S.

$L_{i:V_a k}$ represents interactions between a metal and a neutral; for example $L_{Fe^{+2}V_a C}$ in Fe-C.

$L_{k_1 k_2}$ represents interactions between two neutrals; for example $L_{Si_3 N_4 SiO_2}$ in $Si_3 N_4$ - SiO_2 . It should be noted that the cation is irrelevant here as the number of cation sites has become zero when only neutrals are taken into account.

The model is certainly complex, but perhaps no more so than previous ionic liquid models described in Sections 5.5.1 and 5.5.2. The initial experience (Selleby 1996) suggests that the number of terms needed to describe a ternary system such as Fe-Mn-S is quite similar for both ionic two-sublattice liquid and associate models (see next section). The modelling of ionic liquids is, in the main, complex and the advantages of the various techniques can only become apparent as they become more commonly used.

There are a number of immediate advantages to the two-sublattice ionic liquid model. The first is that it becomes identical to the more usual Redlich-Kister representation of metallic systems when the cation sublattice contains only vacancies. This immediately allows data from an assessed metallic system to be combined with data from an oxide system so that the full range of compositions is covered. In binary cases the model can be made equivalent to an associational model. For example in Cu-S the associated model would consider a substitutional solution of Cu, S and Cu_2S . If an ionic two-sublattice model with a formula $(Cu^{+1})_P(S^{2-})_Q$ is used, it is straightforward to derive parameters to give identical results to the associate model. However, it should be noted that the Gibbs energy of the two models does not remain equivalent if they are extended into ternary and higher-order systems (Hillert *et al.* 1985).

5.5.4 Associated solution models

There are a number of papers dealing with the associated models (Predel and Oehme 1974, Sommer 1977, Sharma and Chang 1979, Chaang *et al.* 1981, Björkman 1985) which are all very similar in principle. There are differences in the way the excess terms are handled, but all consider that some type of complex or associate is formed inside the liquid from a reaction between the components of the system in question. The thermodynamic properties of the liquid then depend predominantly on the Gibbs energy of formation of these complexes, or associates, rather than by interactions between the components. This gives rise to enthalpy of mixing diagrams which are characterised by sharp changes at critical compositions

where the associate(s) exist and also by markedly non-ideal mixing entropies. The derivation of Sommer (1977, 1980, 1982) can be used as an example. This considers the formation of a single associate with a formula $A_i B_j$ within a binary system $A-B$. It is assumed the liquid contains n_{A_1} and n_{B_1} number of moles of 'free' A and B in equilibrium with $m_{A_i B_j}$ number of moles of the associate $A_i B_j$. The mole fractions of A , B and $A_i B_j$, in a binary alloy containing 1 mole of A and B atoms, are then given by the formula

$$x_A = n_{A_1} + i n_{A_i B_j}; \quad x_B = n_{B_1} + j n_{A_i B_j} \quad \text{and} \quad x_{A_i B_j} = n_{A_i B_j} \quad (5.63)$$

The excess Gibbs energy of mixing is then given by the general formula

$$G_{\text{mix}}^{\text{exs}} = G^{\text{ass}} + G^{\text{reg}} \quad (5.64)$$

G^{ass} is the Gibbs energy due to the formation of the associate defined as

$$G^{\text{ass}} = n_{A_i B_j} G_{A_i B_j}^{\circ} \quad (5.65)$$

where $G_{A_i B_j}^{\circ}$ is the Gibbs energy of formation of one mole of the associate. G^{reg} considers the Gibbs energy due to the interactions between the components A and B themselves and with the associate $A_i B_j$ such that

$$G^{\text{reg}} = G_{A,B}^{\text{reg}} \frac{n_{A_1} n_{B_1}}{n} + G_{A,A_i B_j}^{\text{reg}} \frac{n_{A_1} n_{A_i B_j}}{n} + G_{B,A_i B_j}^{\text{reg}} \frac{n_{B_1} n_{A_i B_j}}{n} \quad (5.66)$$

where $n = n_{A_1} + n_{B_1} + n_{A_i B_j}$. The configurational entropy is given simply by

$$S_{\text{mix}}^{\text{conf}} = -R(n_{A_1} \log_e x_A + n_{B_1} \log_e x_B + n_{A_i B_j} \log_e x_{A_i B_j}) \quad (5.67)$$

The model was applied to numerous ionic melts and good agreement was found with experimental results (Sommer 1982). One of the main criticisms of the associate formalism has been that, although the concept considers associates or complexes to be 'diffuse' in nature, the mathematical formalism implies that distinct molecules exist, which is harder to justify. However, if this stringent view is relaxed, it can be seen that the model merely implies some underlying structure to the liquid, which is quite reasonable, and it does provide functions which allow for the temperature dependence of the enthalpy of mixing. A more serious criticism is that some knowledge of the relevant associate is necessary before Eqs (5.64)-(5.67) can be applied. The most appropriate associate can be selected by fitting of experimental results for enthalpies of mixing which is sufficient in a large number of cases. However, in some systems there may be a number of different associates and it is not always obvious as to which types actually exist. The main advantages

References are listed on pp. 124-126.

of the associate models is that they allow a simple strategy to be adopted for optimisation. It is further easy to define ternary and higher-order associates and extend the model to multi-component systems. For example, Björkman (1985) showed this to good effect in the system Fe-O-SiO₂.

To complete this section it is interesting to show the equivalence between the ionic two-sublattice model and the associate model as demonstrated by Hillert *et al.* (1985). Equation (5.62) can be simplified for a system $(A^{+va})_p (B^{+vb}, Va^{-va}, B^{\circ})_q$ where $+va = -vb$ to become, for one mole of atoms,

$$G = \frac{y_B G_{A(-vB/+vA)B_1}^{\circ} + RT(y_B \log_e y_B + y_b \log_e y_b + y_V \log_e y_V a) + G_{\text{mix}}^{\text{exs}}/v_A}{\left(1 - \frac{y_B v_B}{v_A}\right)} \quad (5.68)$$

where y_b is the site fraction occupation of the neutral B° on sublattice B° . Equations (5.65)-(5.67) will yield for one mole of atoms

$$G = \frac{\left(x_{A_i B_j} G_{A_i B_j}^{\text{ass}} + RT(x_{A_i B_j} \log_e x_{A_i B_j} + x_{A_1} \log_e x_{A_1} + x_{B_1} \log_e x_{B_1}) + x_{A_1} x_{B_1} G_{A_1 B_1}^{\text{reg}} + x_{A_1} x_{A_i B_j} G_{A_1 A_i B_j}^{\text{reg}} + x_{B_1} x_{A_i B_j} G_{B_1 A_i B_j}^{\text{reg}} \right)}{(1 + x_{A_i B_j})(i + j - 1)} \quad (5.69)$$

The two models become identical for the case where $i = j = vA = -vB = 1$ and it is then possible to show the following identities: (1) $x_{A_i B_j} \equiv y_B$, (2) $x_{B_1} \equiv y_b$ and (3) $x_{A_1} \equiv y_V a$.

As $y_A = 1$, the G^{reg} term has the following equivalence

$$x_{A_i B_j} G_{A_i B_j}^{\text{ass}} = y_A y_B G_{A^{+va}, B^{-vb}}^{\circ} \quad (5.70)$$

and the excess terms of the associate show the following equivalences

$$\begin{aligned} x_{A_1} x_{B_1} G_{A_1 B_1}^{\text{reg}} &= y_A y_V a y_B L_{A^{+va}, B^{\circ}, Va^{-va}} \\ x_{A_1} x_{A_i B_j} G_{A_1 A_i B_j}^{\text{reg}} &= y_A y_V a y_B L_{A^{+va}, B^{-vb}, Va} \\ x_{B_1} x_{A_i B_j} G_{B_1 A_i B_j}^{\text{reg}} &= y_A y_b y_B L_{A^{+va}, B^{\circ}, B^{-vb}} \end{aligned} \quad (5.71)$$

They can also be made identical in the general case if the conditions $i = -vB/vA$ and $j = 1$. The equivalences break down in ternary and higher-order systems as there is the introduction of more compositional variables in the associate model than for the two-sublattice case. This was considered (Hillert *et al.* 1985) to demonstrate the advantages of the sub-lattice model, but as mentioned previously it turns out that the number of excess terms to describe Fe-Mn-S is very similar.

5.6 AQUEOUS SOLUTIONS

Aqueous solutions form a large area for thermodynamic modelling and hold great importance in their own right. However, they are, by definition, basically dilute solutions and almost all models deal exclusively with the thermodynamic properties of the aqueous solution, only considering some possible precipitation reactions of insoluble, mainly stoichiometric, compounds. The integration of these models into concentrated solution databases which are often used at high temperatures has therefore not been seriously undertaken by any group as far as the authors are aware. There has, however, been quite significant use of aqueous models in conjunction with substance databases for prediction of thermodynamic properties and solubility products in a number of important areas such as corrosion and geochemistry. To this end some discussion of aqueous modelling is worthwhile.

One of the main conceptual differences between the models discussed so far and aqueous solutions is that the units which are used to define thermodynamic functions are often different. This is because they apply to the properties which are actually measured for aqueous systems, and molarity (c_i) and molality (m_i) are far more common units than mole fraction. Molarity is defined as

$$c_i = \frac{10^{-3}n_i}{V} \quad (5.72)$$

and molality as

$$m_i = \frac{n_i}{n_w M_w} \quad (5.73)$$

where M_w is the molar mass of water and V the volume of the solution in m^3 . The partial ideal mixing term for component i , (\bar{G}_i^{ideal}) can be defined with respect to molality as

$$\bar{G}_i^{\text{ideal}} = \bar{G}_i^{\circ} + RT \log_e (m_i) \quad (5.74)$$

where \bar{G}_i° is the chemical potential of component i in its standard state. This can be combined with some term for the partial excess Gibbs energy so that the chemical potential of i can be defined. The excess Gibbs energy term is defined using the ionic strength (I) where

$$I = 0.5 \sum_i m_i z_i^2 \quad (5.75)$$

where z_i is the charge in electron units of the component i . This can be used to define the limiting excess Gibbs energy of an electrolyte solution containing cations of charge z^+ and anions of charge z^- via the Debye-Hückel limiting law as

$$\frac{\bar{G}^{\text{ex}}}{(n_w M_w RT)} = -\frac{4}{3} AI^{3/2} \quad (5.76)$$

References are listed on pp. 124-126.

Differentiation of Eq. (5.76) with respect to the amount of solute leads to the expression

$$\log_e \gamma_i = -z_i^2 A \sqrt{I}. \quad (5.77)$$

The above equation assumes that the ions are point charges and interact in a continuous dielectric. It is essentially correct in the limit, but problems arise when considering finite concentrations of solute where an extended Debye-Hückel expression may be more appropriate

$$\log_e \gamma_i = \frac{-z_i^2 A \sqrt{I}}{(1 + B a_i \sqrt{I})}. \quad (5.78)$$

Here A and B are temperature-dependent parameters which are properties of pure water only and a_i is the effective diameter of the hydrated ion. This expression can be used up to ionic strengths of 5×10^{-2} (Davies 1985) but for higher concentrations further terms are needed. One of the simplest expressions is to consider a linear term with respect to ionic strength such that

$$\log_e \gamma_i = \frac{-z_i^2 A \sqrt{I}}{(1 + B a_i \sqrt{I})} + \beta I \quad (5.79)$$

or, more generally,

$$\log_e \gamma_i = \frac{-z_i^2 A \sqrt{I}}{(1 + B a_i \sqrt{I})} + \sum_j \beta_j I^j. \quad (5.80)$$

By considering $B a_i$ as a single adjustable parameter, data can then be fitted using only $B a_i$ and β as variables. A further simplification is to make $B a_i$ equal to unity and add a further constant ionic strength term which gives the Davies equation (Davies 1962)

$$\log_e \gamma_i = -z_i^2 A \left(\frac{\sqrt{I}}{(1 + \sqrt{I})} - 0.3I \right). \quad (5.81)$$

Further expansions are possible following Bromley (1973) and Zemaitis (1980) such that

$$\log_{10} \gamma_i = \frac{-z_i^2 A \sqrt{I}}{(1 + \sqrt{I})} + \frac{(0.06 + 0.6\beta)z_i^2}{\left(1 + \frac{1.5I}{z_i^2}\right)} + \beta + \chi I^2 + \delta I^3. \quad (5.82)$$

A further approach is to consider a more specific form of ion interaction and replace Eq. (5.80) with the Bronsted-Guggenheim equation (Guggenheim and Turgeon 1955)

$$\log_e \gamma_i = \frac{-z_i^2 A \sqrt{I}}{(1 + B_{a_i} \sqrt{I})} + \sum_j \varepsilon_{(i,j), i_m} m_j \quad (5.83)$$

The last term represents ion interactions between i and j as a function of ionic strength. A simplification of Eq. (5.83) was suggested by Pitzer and Brewer (1961) such that

$$\log_{10} \gamma_i = \frac{-0.5107 z_i^2 \sqrt{I}}{(1 + \sqrt{I})} + \sum_j \varepsilon_{(i,j)} m_j \quad (5.84)$$

where the interaction coefficients become concentration independent. The Debye-Hückel term then has similarities with the Davies equation in that B_{a_i} is made equal to unity.

One of the main models which is available in CALPHAD calculation programmes is that based on Pitzer (1973, 1975), Pitzer and Mayorga (1973) and Pitzer and Kim (1974). The model is based on the development of an explicit function relating the ion interaction coefficient to the ionic strength and the addition of a third virial coefficient to Eq. (5.83). For the case of an electrolyte MX the excess Gibbs energy is given by

$$\frac{G_{\text{mix}}^{xs}}{RT} = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \quad (5.85)$$

with

$$f(I) = \frac{-4A^\phi I \log_e(1 + 1.2\sqrt{I})}{1.2} \quad (5.86)$$

where $\lambda_{ij}(I)$ and μ_{ijk} are second and third virial coefficients from the non-electrostatic part of G_{mix}^{xs} and A^ϕ is the Debye-Hückle limiting slope. μ_{ijk} is taken to be independent of ionic strength and set to zero if ions i , j and k have the same charge sign. Equation (5.86) is similar in form to the excess terms considered for simple mixture phases, except that some specific terms arising from the unique properties of aqueous systems are included. Differentiation of Eq. (5.85) with respect to concentration yield the following expression for activity coefficients of cation (M), anion (X) and neutral species (N) (Clegg and Brimblecombe 1989)

$$\begin{aligned} \log_e \gamma_M = & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \Psi_{Mca} \right) \\ & + \sum_{a < c'} \sum_a m_a m_{a'} \Psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \\ & + 2 \sum_n m_n \lambda_{Mn} + 3 \sum_j \sum_k m_j m_k \mu_{Mjk} \end{aligned} \quad (5.87a)$$

References are listed on pp. 124-126.

$$\begin{aligned} \log_e \gamma_X = & z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a \left(2\Phi_{aX} + \sum_c m_c \Psi_{cXa} \right) \\ & + \sum_{c < c'} \sum_c m_c m_{c'} \Psi_{Xcc'} + |z_X| \sum_c \sum_a m_c m_a C_{ca} \\ & + 2 \sum_n m_n \lambda_{Xn} + 3 \sum_j \sum_k m_j m_k \mu_{Xjk} \end{aligned} \quad (5.87b)$$

$$\log_e \gamma_N = 2 \sum_n m_n \lambda_{Nn} + 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na} + 3 \sum_i \sum_j m_i m_j \mu_{Nij} \quad (5.87c)$$

where the subscripts c , a , and n represent cations, anions and neutrals respectively. Summation indices $c < c'$ and $a < a'$ denote sums over all distinguishable pairs of cations and anions while summations with indices i , j and k cover all species and are unrestricted. $Z = \sum_i m_i |z_i|$ while F is defined as

$$\begin{aligned} F = & -A^\phi \left(\frac{\sqrt{I}}{(1 + b\sqrt{I})} + \frac{2 \log_e(1 + b\sqrt{I})}{b} \right) + \sum_c \sum_a m_c m_a B'_{ca} \\ & + \sum_{c < c'} \sum_c m_c m_{c'} \Phi'_{cc'} + \sum_a \sum_{a < a'} m_a m_{a'} \Phi'_{aa'} \end{aligned} \quad (5.88)$$

The ionic strength dependence of the coefficients, B_{MX} , is

$$B_{MX}^\phi = \beta_{MX}^0 + \beta_{MX}^1 \exp(-\alpha\sqrt{I}) \quad (5.89)$$

$$B_{MX} = \beta_{MX}^0 + \beta_{MX}^1 g(\alpha\sqrt{I}) \quad (5.90)$$

$$B'_{MX} = \frac{\beta_{MX}^1 g'(\alpha\sqrt{I})}{I} \quad (5.91)$$

with the function g and g' given by

$$g = \frac{2 \left(1 - (1 + \alpha\sqrt{I}) \exp(-\alpha\sqrt{I}) \right)}{\alpha^2 I} \quad (5.92a)$$

$$g' = \frac{-2 \left(1 - (1 + \alpha\sqrt{I} + \alpha^2 I/2) \exp(-\alpha\sqrt{I}) \right)}{\alpha^2 I} \quad (5.92b)$$

where α is usually assigned a value of 2 for electrolytes of low charge. The mixture terms Φ^ϕ , Φ and Φ' are defined as

$$\Phi_{ij}^0 = \theta_{ij} + {}^E\theta_{ij}(I) + I^E\theta'_{ij}(I) \quad (5.93)$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (5.94)$$

$$\Phi'_{ij} = {}^E\theta'_{ij}(I) \quad (5.95)$$

θ_{ij} is a constant for each pair of ions. ${}^E\theta_{ij}(I)$ and ${}^E\theta'_{ij}(I)$ are universal functions that are required when ions of differing charge types are mixed.

As can be seen from the above equations, modelling of concentrated aqueous solutions becomes complex and it is not possible within the scope of this book to do justice to what is a major field in its own right. There are a number of articles which can be recommended to give the reader some idea of what can be achieved with aqueous models. Harvie and Weare (1980) developed a model for calculating mineral solubilities in natural waters based on the Pitzer equations which achieved good accuracy up to strengths of 20 m. This work was extended by Harvie *et al.* (1982, 1984) so that a database exists for the prediction of mineral solubilities in water up to high ionic strengths at 25°C for the system Na, K, Mg, Ca, H, Cl, SO₄, OH, HCO₃, CO₃, CO₂, H₂O. More recently Clegg and Brimblecombe (1989) presented a database, again using the Pitzer model, for the solubility of ammonia in aqueous and multi-component solutions for the system Li, Na, Mg, NH₄, Mg, Ca, Sr, Ba, F, Cl, Br, I, OH, CNS, NO₃, ClO₄, S, SO₃, CH₃COO, HCOO and (COO)₂, H₂O. Further models and applications can be found in articles by Zematits (1980) and Grenthe and Wanner (1988). The review of Davies (1985) also gives details of software programmes which are available for calculating equilibria in aqueous solutions.

REFERENCES

- Ansara, I. (1979) *Int. Met. Reviews*, **22**, 20.
 Ansara, I. and Sundman, B. (1987) in *Computer Handling and Dissemination of Data*, ed. Glaeser, P. S., p. 154. CODATA.
 Ansara, I., Sundman, B. and Willemín, P. (1988) *Acta Metall.*, **36**, 977.
 Ansara, I., Bernard, C., Kaufman, L. and Spencer, P. (1978) *CALPHAD*, **2**, 1.
 Ansara, I., Chart, T. G., Hayes, F. H., Pettifor, D. G., Kattner, U., Saunders, N. and Zeng, K. (1997) *CALPHAD*, **21**, 171.
 Bale, C. W. and Pelton, A. D. (1990) *Met. Trans. A*, **21A**, 1997.
 Bhadeshia, H. K. D. H. (1981) *Metal Science*, **15**, 175.
 Björkman, B. (1985) *CALPHAD*, **9**, 271.
 Blander, M. and Pelton, A. D. (1984) in *Second International Symposium on Metallurgical Slags & Fluxes*, eds Fine, A. H. and Gaskell, D. R. (Met. Soc. AIME, New York), p. 295.
 Bragg, W. L. and Williams, E. J. (1934) *Proc. Roy. Soc.*, **A145**, 69.
 Bromley, L. A. (1973) *J. Amer. Inst. Chem. Eng.*, **19**, 313.
 Chuang, Y.-Y., Hsieh, K.-C. and Chang, Y. A. (1981) *CALPHAD*, **5**, 277.
 Clegg, S. L. and Brimblecombe, P. (1989) *J. Phys. Chem.*, **93**, 7237.
 Colinet, C. (1967) D.E.S. University of Grenoble, France.
 Davies, C. W. (1962) *Ion Association* (Butterworths, Washington).
 Davies, R. H. (1985) in *Critical Thermodynamics in Industry: Models and Computation*, ed. Barry, T. I. (Blackwell Scientific, Oxford), p. 40.
 Dinsdale, A. T. (1991) *CALPHAD*, **15**, 317.
 Dupin, N. (1995) Ph.D. Thesis, l'Institut National Polytechnique de Grenoble, France.
 Enomoto, M. and Aaronson, H. I. (1985) *CALPHAD*, **9**, 43.
 Eriksson, G., Wu, P. and Pelton, A. D. (1993) *CALPHAD*, **17**, 189.
 Flood, H. *et al.* (1954) *Z. Anorg. Allg. Chem.*, **276**, 289.
 Foo, E.-H. and Lupis, C. H. P. (1975) *Acta Met.*, **21**, 1409.
 Fowler, R. H. and Guggenheim, E. A. (1939) *Statistical Thermodynamics* (Cambridge University Press, Cambridge).
 Gaye, H. and Welfringer, J. (1984) in *Proceedings of Second Symposium on Metallurgical Slags and Fluxes*, eds Fine, H. A. and Gaskell, D. R. (Met. Soc. AIME, New York), p. 357.
 Grenthe, I. and Wanner, H. (1988) *Guidelines for the extrapolation to zero ionic strength*, Report TDB-2 to OECD Nuclear Energy Agency, Data Bank, F-91191 Gif-sur-Yvette, France (December 5, 1988).
 Gros, J. P. (1987) Dr. Ing. Thesis, l'Institut National Polytechnique de Grenoble, France.
 Guggenheim, E. A. (1935) *Proc. Roy. Soc.*, **A148**, 304.
 Guggenheim, E. A. and Turgeon, J. C. (1955) *Trans. Farad. Soc.*, **51**, 747.
 Harvie, C. E. and Weare, J. H. (1980) *Geochim. Cosmochim. Acta*, **44**, 981.
 Harvie, C. E., Eugster, H. P. and Weare, J. H. (1982) *Geochim. Cosmochim. Acta*, **46**, 1603.
 Harvie, C. E., Møller, N. and Weare, J. H. (1984) *Geochim. Cosmochim. Acta*, **48**, 723.
 Harvig, H. (1971) *Acta Chem. Scand.*, **25**, 3199.
 Hillert, M. (1980) *CALPHAD*, **4**, 1.
 Hillert, M. and Steffansson, L.-I. (1970) *Acta Chem. Scand.*, **24**, 3618.
 Hillert, M. and Waldenstrom, M. (1977) *CALPHAD*, **1**, 97.
 Hillert, M., Jansson, B., Sundman, B. and Ågren, J. (1985) *Met. Trans. A*, **16A**, 261.
 Hoch, M. and Appshofen, M. (1984) *Z. Metallkde.*, **75**, 23 and 30.
 Inden, G. (1975a) *Z. Metallkde.*, **66**, 577.
 Inden, G. (1975b) *Z. Metallkde.*, **66**, 648.
 Inden, G. (1977a) *Z. Metallkde.*, **68**, 529.
 Inden, G. (1977b) *J. de Physique. Colloque*, **C7**, 373.
 Kapoor, M. L. and Froberg, G. M. (1973) in *Chemical Metallurgy of Iron and Steel* (Iron and Steel Institute, London), p. 17.
 Kaufman, L. and Bernstein, H. (1970) *Computer Calculation of Phase Diagrams* (Academic Press, New York).
 Kaufman, L. and Nesor, H. (1978) *CALPHAD*, **2**, 35.
 Kirkaldy, J. S., Thomson, B. A. and Baganis, E. A. (1978) in *Hardenability Concepts with Applications to Steel*, eds Kirkaldy, J. S. and Doane, D. V. (AIME, Warrendale), p. 82.
 Kohler, F. (1960) *Monatsh. Chem.*, **91**, 738.
 Lupis, C. H. P. and Elliott, C. H. P. (1966) *Acta Met.*, **4**, 529 and 1019.
 Masson, C. R. (1965) *Proc. Roy. Soc.*, **A287**, 201.
 Muggianu, Y. M., Gambino, M. and Bros, J. P. (1975) *J. Chim. Phys.*, **22**, 83.