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The compound energy formalism

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Abstract

The compound energy formalism for solution phases with sublattices is very flexible and thermodynamic models for a large variety of phases have been constructed within this formalism. The range of applications is reviewed and the methods of handling various problems are examined. Recent developments including treatments of short range order within the compound energy formalism are reviewed.

Keywords: Sublattice; Compound; Solution; Thermodynamics; Modelling

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1. Introduction

Ever since the thermodynamic treatments of lattice defects in stoichiometric phases by Wagner and Schottky in 1930 [1] and Ölander in 1932 [2] and of interstitial solutions by Johansson in 1937 [3], it has been realized that an adequate description of the properties of solution phases with sublattices must take the existence of the sublattices into account. Initially, most of the interest was focused on low contents of defects or interstitials but the need to cover the whole range of composition has grown as an effect of the CALPHAD approach which started by the introduction of the concept ‘lattice stability’ [4] in order to describe the whole composition range for substitutional solutions. The concept of ‘compound energy’ plays the same role for solution phases with sublattices as ‘lattice stability’ plays for substitutional solutions.

There have been many efforts to develop physical models of the interactions between atoms in sublattice phases, e.g. the Bragg–Williams model [5]. The compound energy formalism started [6] as a purely mathematical method, based on an analytical expression for the Gibbs energy using terms of increasing powers of the mole fractions of atoms within the individual sublattices, so-called ‘site fractions’. In addition, random mixing within each sublattice was assumed when constructing the terms for the constitutional entropy. It is thus the natural extension of the regular solution model with higher power terms and it reduces to that model when all the sites in all but one of the sublattices are vacant.

The compound energy formalism has been applied to the modelling of a large variety of phases and methods have been developed to treat different situations. These methods will now be reviewed and examined.

2. Definition of the compound energy formalism

The compound energy formalism [6–9] was constructed in order to describe models of the thermodynamic properties of phases with two or more sublattices which show a variation in composition, i.e. belonging to the class of solution phases. The structure of a phase is represented simply by the formula, e.g. $(A,B)_k(D,E,F)_l$ where A and B mix on the first sublattice and D, E and F mix on the second one. The coefficients k and l are the stoichiometric coefficients and one mole of formula units thus contains $k+l$ moles of atoms. The general notation for the stoichiometric coefficients will be n^s where the superscript s defines the sublattice. The constitution of the phase is described by the site fractions, y_A^s, etc. Thus, the summation over each sublattice yields $\Sigma y_J^s=1$, etc. It should be noted that J can represent any type of species, i.e. atom, molecule, ion or vacancy. A certain species in a certain sublattice is regarded as a ‘constituent’. A component I of a phase can occur as a constituent in more than one sublattice, i.e. as more than one constituent of the phase. It may even occur in more than one constituent in the same sublattice. As an example, the component Fe may occur as Fe^{+2} and Fe^{+3} and O may occur in SO_3^{-2} and SO_4^{-2}. When

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all the constituents are single atoms, simple ions or vacancies, the number of atoms per formula unit will be $\Sigma n^s(1-y^s_{Va})$.

In the limits there will be only one species on each sublattice, and stoichiometric compounds are thus defined as 'end-members of the solution phase' or simply 'end-member compounds', e.g. A_kD_l. For simplicity, the symbol for the Gibbs energy of an end-member will be given by giving the element on each sublattice but excluding the stoichiometric coefficients, e.g. $^\circ G_{A:D}$. The basis of the compound energy formalism is the assumption that, in addition to a term for the ideal entropy of mixing,

$$-S^{mix}_m T = RT\,\Sigma\Sigma\, n^s y^s_J \ln(y^s_J) \quad (1)$$

constructed under the assumption of random mixing within each sublattice, there is a surface of reference (s.r.) defined by

$$G^{s.r.}_m = \Sigma {}^\circ G_{end} \Pi y^s_J \quad (2)$$

where the summation covers all the end-members and the product Πy^s_J contains one site fraction from each sublattice and they are identified by the constituents in the end-member. $^\circ G_{end}$ is the Gibbs energy of one mole of formula units of the compound representing the end-member. The quantity $\Sigma(\Pi y^s_J)$ is unity and $G^{s.r.}_m$ thus represents a weighted average over all the end-members. For a simple case Eq. (2) may be justified by the Bragg and Williams model, which was based on Bethe's proposal of pair-wise bond energies [10], but simplified by replacing Bethe's quasi-chemical approach with random mixing within each sublattice [5]. It is more difficult to justify when different sites have different coordination numbers. The name 'compound energy model' was introduced [9] when it was proposed that Eq. (2) could be used in such cases as well. The name 'compound energy formalism' was later introduced as a more general concept, the idea being that a large variety of models with different physical backgrounds may be expressed in this formalism. A great advantage of a common formalism is that one can develop a general type of software allowing new models to be developed and directly applied as long as they fit into the same formalism. When that is true, it is sufficent to define a model by giving a formula showing the constituents in each sublattice and the number of sites, e.g. $(A,B)_k(D,E,F)_l$.

Numerical values of $^\circ G_{end}$ can only be given relative to standard states (stst) of the components I. Using such states one can define the Gibbs energy of formation as

$$\Delta_f {}^\circ G_{end} = {}^\circ G_{end} - \sum {}^\circ G^{stst}_I \sum m^s \quad (3)$$

where the first summation covers all the components I present in the end-member and m^s is the number of I atoms present in sublattice s of the end-member. It should be noted that, when $^\circ G_{end}$ from Eq. (3) is inserted in Eq. (2), one gets $\Sigma\Delta_f {}^\circ G_{end}\Pi y^s_J$ but also an expression we can give in the following condensed form $\Sigma {}^\circ G^{stst}_I\, \Sigma y^s_J m^s$ where J represents all constituents containing component I.

When there are no complex constituents, J is identical to I and m^s is identical to n^s, and for each component I one obtains a term $^\circ G^{stst}_I\, \Sigma y^s_I n^s$ where the summation covers all the sublattices containing the component I as a constituent. The content of a component I per mole of formula units would then be related to the mole fraction of I, x_I, through the number of atoms per formula unit,

$$\sum(n^s y^s_I) = x_I \sum n^s(1-y^s_{Va}). \quad (4)$$

What remains in excess of these contributions to the Gibbs energy is usually regarded as excess terms and they are described with a generalized regular solution expression,

$$^E G_m = \Pi y^s_J \sum y^t_B L_{A,B:D:G\,...} + \Pi y^s_J \sum\sum y^t_B y^u_D L_{A,B:D,E:G\,...} + \,... \quad (5)$$

The commas in the subscripts separate constituents within a sublattice and the colons separate constituents in different sublattices. As before, the products cover one constituent on each sublattice. In the first group of terms, the summation covers a second constituent in one sublattice at a time and the L parameters are thus identified. In the second group of terms, the double summation covers additional constituents in two sublattices. The latter parameters are often called 'reciprocal parameters'. The L parameters could depend on composition and Redlich–Kister terms in site fractions are recommended [11]. After rearrangement, the complete expression per mole of formula units would thus be

$$G_m - \sum n^s(1-y^s_{Va}) \sum x_I {}^\circ G^{stst}_I = \sum \Delta_f {}^\circ G_{end} \Pi y^s_J + RT \sum\sum n^s y^s_J \ln(y^s_J) + {}^E G_m. \quad (6)$$

The left hand side represents the mixing Gibbs energy, $^M G_m$. When each component only occurs as a single species and it only resides in one sublattice, Eq. (4) could be inverted and each y^s_I could be calculated directly from the corresponding x_I. However, in the general case there are more independent site fractions than mole fractions and for a given composition one would have to minimize G_m with respect to all the site fractions in order to find the equilibrium values of all the site fractions. The relations given by Eq. (4) would then have to be used as auxiliary conditions. For phases containing ions it is also necessary to use the condition of electroneutrality as an auxiliary condition. This kind of calculation is available in programs for thermodynamic calculations, e.g. Thermo-Calc [12]. It is only necessary to define the formula for the phase and then to give the model parameters, i.e. all the $\Delta_f {}^\circ G$ and L quantities, unless they are already stored in a database directly accessible for the program.

The bond energy model is constructed for phases where atoms in different sublattices have the same coordination number and it can then be brought into the compound energy formalism. On the other hand, it is not evident how a bond energy model can be formulated when the coordination number is different for different sites but the compound energy formalism, being a purely mathematical model, can be applied directly to such cases as well. However, as discussed in Section 7, one may then need to consider the introduction of excess terms.

3. A simple reciprocal solution phase

In order to illustrate the compound energy formalism it is convenient to use the simple case $(A,B)_l(D,E)_l$. All possible compositions can be represented on a square with the axes y^t_B and y^u_E. It may be called 'composition square'. Even though there are four end-members, it is evident that any composition can be obtained by mixing three end-members. In particular, the center of the square may be obtained by mixing equal amounts of either A:D and B:E or A:E and B:D. This is why one calls $(A,B)_l(D,E)_l$ a reciprocal solution phase.

One can plot the surface of reference perpendicular to the composition square, Fig. 1, and this would approximate the whole Gibbs energy if there is no excess term and the temperature is low enough to make the ideal entropic contribution negligible. It is evident that an alloy of the central composition would decrease its Gibbs energy by separating into two parts, one consisting of A:D and the other of B:E. The driving force for this demixing is $0.25\Delta^\circ G_{A,B:D,E}$ where

$$\Delta^\circ G_{A,B:D,E} = {}^\circ G_{A:E} + {}^\circ G_{B:D} - {}^\circ G_{A:D} - {}^\circ G_{B:E} \qquad (7a)$$

It can also be given as

$$\Delta^\circ G_{A,B:D,E} = \Delta_f {}^\circ G_{A:E} + \Delta_f {}^\circ G_{B:D} - \Delta_f {}^\circ G_{A:D} - \Delta_f {}^\circ G_{B:E} \qquad (7b)$$

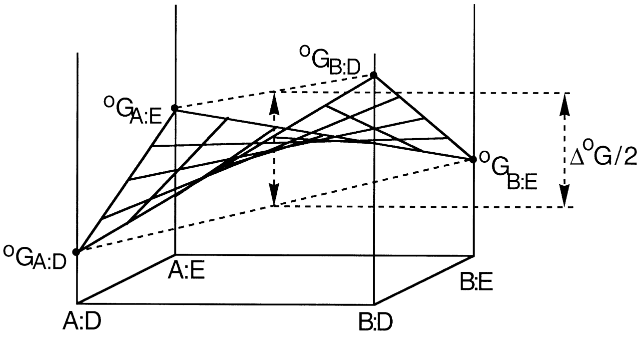

Fig. 1. The surface of reference for the Gibbs energy of a phase $(A,B)_1(C,D)_1$, according to the compound energy formalism, plotted above the composition square.

because each standard state is eliminated. We shall regard this as the 'reaction parameter'.

At realistic temperatures the ideal entropic contribution will modify the tendency of demixing and the miscibility gap will close at some critical temperature. By symmetry reasons, the critical point, i.e. the point of maximum on the miscibility gap, will fall in the center in this simple case and its temperature can be found as follows. Start with the molar Gibbs energy expression,

$$G_m = y^t_A y^u_D\, {}^\circ G_{A:D} + y^t_B y^u_D\, {}^\circ G_{B:D} + y^t_A y^u_E\, {}^\circ G_{A:E} + y^t_B y^u_E\, {}^\circ G_{B:E} + RT \sum \sum y^s_J \ln(y^s_J) \qquad (8)$$

For variations parallel to the A:D–B:E diagonal we have $dy^t_A = -dy^t_B = -dy^u_E = dy^u_D$ and obtain

$$d^2 G_m / d(y^u_E)^2 = 2{}^\circ G_{A:D} - 2{}^\circ G_{B:D} - 2{}^\circ G_{A:E} + 2{}^\circ G_{B:E} + RT_{cr} \sum \sum (1/y^s_J) = 0 \qquad (9)$$

For symmetry reasons we can insert all $y_J = 1/2$ at the critical (consolute) point, obtaining

$$T_{cr} = \Delta^\circ G_{A,B:D,E} / 4R \qquad (10)$$

If $\Delta^\circ G_{A,B:D,E}$ is negative, one would obtain an identical result for a miscibility gap parallel to the A:E–B:D diagonal. It is thus typical of reciprocal solution phases that there is always a tendency of demixing in one direction or the other.

4. Chemical potentials

Except for the very simplest case, it would be very difficult to carry out numerical calculations without a computer program. The program should be able to perform calculations of all thermodynamic properties and in publications there would be no need to present equations except for the Gibbs energy which is used for storing the basic thermodynamic information. Nevertheless, it may be of interest here to discuss the analytical calculation of chemical potentials. For a phase with sublattices they are primarily defined for compounds, the end-members, and not for components or constituents. See [13], for instance. The chemical potential for a compound $A_kD_lG_m$ would be obtained as

$$\mu_{A:D:G} = G_m + \partial G_m/\partial y^t_A + \partial G_m/\partial y^u_D + \partial G_m/\partial y^v_G - \sum \sum (y^s_J \partial G_m / \partial y^s_J) \qquad (11)$$

By definition, this quantity is related to the chemical potentials of the constituents by

$$\mu_{A:D:G} = k\mu_A + l\mu_D + m\mu_G \qquad (12)$$

5. Vacancies

There are many cases where vacancies enter into one of the sublattices. The corresponding end-members will then be represented by compounds with an empty sublattice. In the simple case of two sublattices these compounds will be A_kVa_l, etc. which is identical to k atoms of pure A in the related structure, i.e. with all the sites in the second sublattice empty. It may be a stable, metastable or unstable state of the element. In this case, the chemical potential of 'the compound' A_kVa_l is identical to $k\mu_A$ because the chemical potential of vacancies is zero at so-called thermal equilibrium. It is also possible to obtain the chemical potential of a constituent in the sublattice with vacancies using Eq. (12) for a phase with two sublattices,

$$\mu_{A:D} - \mu_{A:Va} = k\mu_A + l\mu_D - k\mu_A - l\mu_{Va} = l\mu_D - l\mu_{Va} = l\mu_D \qquad (13)$$

If the practical interest in the phase lies in the region of low content of all the atoms in the sublattice with vacancies, then one talks about an interstitial solution, in particular if there are only two sublattices, one for substitutional alloy elements and one for interstitials.

Fig. 2 illustrates all possible constitutions for the simple case of $(A,B)_1(B,Va)_1$. A constant composition is no longer limited to a point but can exist on a straight line. Along that line the constitution, i.e. the distribution over different sublattices, varies. Thus, the square is no longer a true composition square but for the sake of simplicity we shall retain that name. The full line holds for the 50/50 composition and has a slope of 2. This is an example where the equilibrium constitution can only be found by minimizing G_m.

6. Anti-sites and ordering

One talks about anti-sites when an element, that normally resides in one sublattice, dissolves to a lower extent in another sublattice. That model can be directly included in the compound energy formalism. Let us consider a binary phase with two sublattices where A prefers the first one and B the second one, a fact indicated by the positions and the use of bold letters in the example $(\mathbf{A},B)_1(\mathbf{B},A)_2$. (Except for this purpose, the recommendation to arrange the constituents of each sublattice in alphabetical order will be followed in the present review. It has an effect on the signs of Redlich–Kister parameters.) In general, the amount of anti-site atoms will increase at increasing temperature due to the effect of the configurational entropy. The phase will be more and more disordered. We shall now examine if there is an order-disorder transition at some critical temperature where the phase disorders completely. The material balance for the phase $(A,B)_1(B,A)_2$ requires that an alloy of given composition falls on a line with the slope 1/2 in Fig. 3. The full line holds for the 50/50 composition. The completely disordered states would be represented by the intersection between the line for each alloy composition and the diagonal A_1A_2–B_1B_2 (dotted line) because there $y_A^u = 1 - y_B^t$, i.e. y_A^t. It is thus necessary that the G_m curve in the section for constant composition can have a minimum at that intersection,

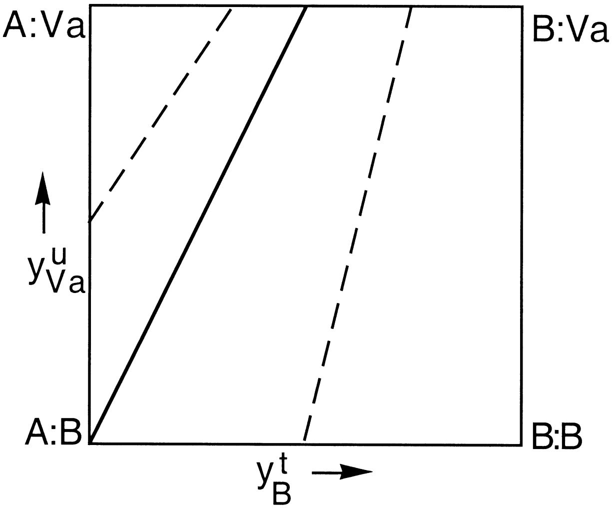

Fig. 2. The so-called composition square for a phase $(A,B)_1(B,Va)_1$, representing all possible constitutions. All constitutions on the full line can form from the same composition, 50% A, 50% B. The dashed lines hold for two other compositions.

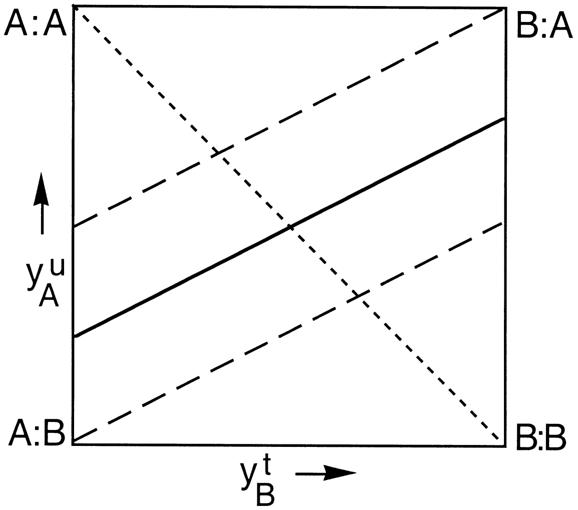

Fig. 3. The so-called composition square for a phase $(A,B)_1(B,A)_2$, representing all possible constitutions. Each one of the full and dashed lines represents possible constitutions for a certain composition. In this case the lines are parallel. The full line holds for 50% A, 50% B. Intersections with the dotted line represent completely disordered cases.

otherwise the completely disordered state could never be stable. For the general case, $(A,B)_P(A,B)_Q$, the compound energy formalism yields

$$\begin{aligned} G_m = {} & y^t_A y^u_A {}^\circ G_{A:A} + y^t_A y^u_B {}^\circ G_{A:B} + y^t_B y^u_A {}^\circ G_{B:A} \\ & + y^t_B y^u_B {}^\circ G_{B:B} \\ & + RTP \sum y^t_J \ln(y^t_J) + RTQ \sum y^u_J \ln(y^u_J) + {}^E G_m \end{aligned} \tag{14}$$

For variations of the site fractions under constant composition we have $P\,dy^t_A = -P\,dy^t_B = -Q\,dy^u_A = Q\,dy^u_B$ and from Eq. (14) we get by neglecting ${}^E G_m$,

$$\begin{aligned} Q \cdot \partial G_m / \partial y^t_A = {} & (Qy^u_A - Py^t_A)^\circ G_{A:A} + (Qy^u_B + Py^t_A)^\circ G_{A:B} \\ & - (Qy^u_A + Py^t_B)^\circ G_{B:A} - (Qy^u_B - Py^t_B)^\circ G_{B:B} \\ & + RTQP[1 + \ln(y^t_A) - 1 - \ln(y^t_B)] \\ & + RTQP[-1 - \ln(y^u_A) + 1 + \ln(y^u_B)] \end{aligned} \tag{15}$$

For a disordered state $y^t_A = y^u_A = x_A$ and $y^t_B = y^u_B = x_B$ and the expression must be zero for a minimum in G_m, yielding

$$\begin{aligned} Q \cdot \partial G_m / \partial y^t_A = {} & (Q - P)x_A {}^\circ G_{A:A} + (Qx_B + Px_A)^\circ G_{A:B} \\ & - (Qx_A + Px_B)^\circ G_{B:A} - (Q - P)x_B {}^\circ G_{B:B} \\ = {} & 0 \end{aligned} \tag{16}$$

In order for this to occur over a range of compositions, two conditions must be fulfilled,

$$(Q - P)^\circ G_{A:A} + P\,{}^\circ G_{A:B} - Q\,{}^\circ G_{B:A} = 0 \tag{17}$$

$$Q\,{}^\circ G_{A:B} - P\,{}^\circ G_{B:A} - (Q - P)^\circ G_{B:B} = 0 \tag{18}$$

They can be transformed into the following two conditions

$${}^\circ G_{A:B} = (P\,{}^\circ G_{A:A} + Q\,{}^\circ G_{B:B})/(P + Q) \tag{19}$$

$${}^\circ G_{B:A} = (Q\,{}^\circ G_{A:A} + P\,{}^\circ G_{B:B})/(P + Q) \tag{20}$$

These expressions imply that the energies of the compounds A_PB_Q and B_PA_Q should be exactly equal to the weighted averages of pure A and B in the states of A_PA_Q and B_PB_Q. This can hardly be expected. Consequently, one should not expect that such a phase can disorder completely except by the action of ${}^E G_m$ in Eq. (14) which was later neglected and did not show up in Eqs. (19) and (20). The effect of the excess term will be described in Section 7 but we can already conclude that the coefficients in ${}^E G_m$ must be closely related to the four compound energies in order for this to occur. Otherwise it would be extremely unlikely that their combined effect should give a minimum of G_m exactly for the disordered state. A case of such a relation is the $L1_2$ structure which may be described as A_1B_3. It may disorder completely to the A1 structure because the excess term is due to nearest neighbour bonds within the second sublattice which are exactly like those between the two sublattices.

There is an important exception to the above conclusions. For the case $P = Q$, two of the terms in Eq. (16) become zero and the equation can be satisfied by a single condition, ${}^\circ G_{A:B} = {}^\circ G_{B:A}$, which would occur if the sites in both sublattices were identical. For such structures we can thus expect an order–disorder transition at a temperature between those where G_m has a minimum or a maximum for the disordered state. That temperature is thus obtained by putting the second derivative of G_m to zero. For the 50/50 composition we obtain a result similar to Eq. (10),

$$T_{tr} = \Delta^\circ G_{A,B:B,A}/4R \tag{21}$$

where $\Delta^\circ G_{A,B:B,A} = {}^\circ G_{A:A} + {}^\circ G_{B:B} - {}^\circ G_{A:B} - {}^\circ G_{B:A}$. With this model, the compound energy formalism has thus given the same result as the Bragg–Williams treatment of order–disorder in the B2 structure with the interaction energy $\nu_{AB} = -\Delta^\circ G_{A,B:B,A}/2zN^A$ where N^A is the Avogadro number and z is the coordination number, being 8 for the B2 structure.

In order to indicate if an order–disorder transition is crystallographically possible between two sublattices, it has been proposed [14] that they should be marked with the same type of parenthesis in the formula, as in the following example, [A,B][A,B](D,E). In that case there are three sublattices at low temperatures but there could be complete disorder between the first two, if the temperature is increased above a transition temperature. In view of the above discussion, one would normally expect the number of sites to be the same in the two sublattices taking part in an order→disorder transition. In the following more complicated example, [A,B][A,B]{D,E}{D,E}, there are four sublattices at low temperatures but there could be complete disorder between the first two and also between the last two. It would then be an interesting question whether there will be two different transition temperatures for the two order-disorder reactions or a common one. In the compound energy formalism, the answer would be found by examining the Gibbs energies of the end-members. For instance, if ${}^\circ G_{A:B:D:E}$ and ${}^\circ G_{A:B:E:D}$ have different values, then ordering on the first two sublattices would be affected by ordering on the last two and they would have a common transition temperature.

7. The role of excess terms

The terms of the surface of reference in Eq. (2) represent interactions between atoms on different sublattices because they contain site fractions from different sublattices. The excess terms in the first summation of Eq. (5) contain two site fractions from the same sublattice and would thus be used to represent interactions between atoms in the same sublattice. For most models one would primarily hope that excess terms are small and, as a first approximation, one would neglect them. This may be justified if all the nearest neighbours to an atom are in other sublattices. The terms in the surface of reference would then be the most important ones. However, already when the name 'compound energy model' was proposed [9], it was emphasized that an excess term should be added in case some of the nearest neighbours to an atom are in the same sublattice as the atom itself. This problem was again considered in a more recent discussion of the properties of the compound energy model [15] and the model parameters were there evaluated by counting the bonds and multiplying with bond energies. This may thus be regarded as a way of expressing the Bragg–Williams model in the compound energy formalism. In the special case of $L1_2$ (e.g. $AlNi_3$), where all the atoms have the same coordination number but two thirds of the nearest neighbours to atoms in the second sublattice are in the same sublattice, the compound energy formalism with two sublattices yielded

$$\begin{aligned}{}^{M}G_{m} &= y^{t}_{A}y^{u}_{B}\,\Delta_f{}^{\circ}G_{A:B} + y^{t}_{B}y^{u}_{A}\,\Delta_f{}^{\circ}G_{B:A} \\ &\quad + RT\big[y^{t}_{A}\ln(y^{t}_{A}) + y^{t}_{B}\ln(y^{t}_{B}) + 3y^{u}_{A}\ln(y^{u}_{A}) \\ &\quad + 3y^{u}_{B}\ln(y^{u}_{B})\big] + y^{t}_{A}y^{u}_{A}y^{u}_{B}L_{A:A,B} + y^{t}_{B}y^{u}_{A}y^{u}_{B}L_{B:A,B} \qquad (22)\end{aligned}$$

$\Delta_f{}^{\circ}G_{A:A}$ and $\Delta_f{}^{\circ}G_{B:B}$ disappeared because the standard states were chosen as pure A or B of the same structure. By counting the bonds within the second sublattice and assuming constant bond energies the following relations were obtained.

$$\Delta_f{}^{\circ}G_{A:B} = \Delta_f{}^{\circ}G_{B:A} = N^{A}\,z\nu_{AB} \qquad (23)$$

$$L_{A:A,B} = L_{B:A,B} = (n^{u}/n^{t} - 1)\,\Delta_f{}^{\circ}G_{A:B} = 2\,\Delta_f{}^{\circ}G_{A:B} \qquad (24)$$

because $n^{t}=1$ and $n^{u}=3$ for $AlNi_3$. Thus, there would be only one independent model parameter, represented by $\Delta_f{}^{\circ}G_{A:B}$ or ν_{AB}, both of which are negative when there is a tendency for ordering. This description of the Bragg–Williams model using two sublattices is equivalent to the ordinary treatment of the Bragg–Williams model for the $L1_2$ phase using four equivalent sublattices without interactions within any of them. It may be added that the relations given by Eqs. (23) and (24) would allow G_m to have a minimum in the disordered state, as discussed in Section 6.

This has been an example of the advantage of combining the compound energy formalism, which is purely mathematical, with a physical model in order to derive useful relations between various model parameters.

Another way to handle the presence of nearest neighbour bonds within a sublattice would be to avoid such a situation by splitting that sublattice, if nearest neighbour bonds within all sublattices can thus be avoided. Evidently, that is what the Bragg–Williams model does with four sublattices in the case of $L1_2$. In order to use the compound energy formalism in that way, one must derive the relations between ${}^{\circ}G_{A:A:A:B}$, ${}^{\circ}G_{A:A:B:B}$ and ${}^{\circ}G_{A:B:B:B}$ in terms of the bond energies. As shown, e.g. by Sundman and Mohri [16],

$$\begin{aligned}\Delta_f{}^{\circ}G_{A:A:A:B} &= (3/4)\,\Delta_f{}^{\circ}G_{A:A:B:B} = \Delta_f{}^{\circ}G_{A:B:B:B} \\ &= 12N^{A}\nu_{AB} \qquad (25)\end{aligned}$$

The two four-sublattice treatments, the Bragg–Williams treatment and the one based on the compound energy formalism, are then identical and they are more general than the two-sublattice model. They are very useful for the Au–Cu system where three ordered phases based on the f.c.c. structure appear, Au_3Cu and $AuCu_3$ with the $L1_2$ structure and Au_1Cu_1 with the $L1_0$ structure. However, they need further refinement in order to give realistic results [17].

If all nearest neighbour bonds are taken care of in one of these ways, the remaining part of ${}^{E}G_m$ would primarily represent contributions from next-nearest neighbour bonds. It should be realized that there are cases where they are also quite important. In the case of the B2 structure, there are eight nearest neighbours in the other sublattice but six neighbours in the same sublattice and they are only 15% further away. The energies of such bonds could then have an effect on the structure of the ordered phase.

Ansara, Sundman and Willemin [18] recently discussed a formal way of predicting an order–disorder transition starting from a description of the ordered phase, using excess terms. They pointed out that a disordered state can be stable only if the Gibbs energy, as function of the distribution over different sublattices under constant composition (e.g. as function of y^{t}_{B} for a binary two-sublattice phase) is a point of extremum for the disordered arrangement (i.e. at $y^{t}_{B}=y^{u}_{B}=x_{B}$). As already mentioned in Section 6, this condition will directly give constraints relating the model parameters to each other and they require excess terms if the number of sites on the sublattices are different. This will now be worked out in detail.

By introducing the regular solution parameters, ${}^{\circ}L_{A,B:A}$, ${}^{\circ}L_{A,B:B}$, ${}^{\circ}L_{A:A,B}$ and ${}^{\circ}L_{B:A,B}$, three constraints will be obtained using the method proposed by Ansara et al. They can be written as follows,

$${}^{\circ}L_{A:A,B} = ({}^{\circ}L_{A,B:A} + \Delta_f{}^{\circ}G_{B:A})(n^{u}/n^{t}) - \Delta_f{}^{\circ}G_{A:B} \qquad (26)$$

$$\begin{aligned}{}^{\circ}L_{B:A,B} &= {}^{\circ}L_{A,B:A}(n^{u}/n^{t}) + \Delta_f{}^{\circ}G_{A:B}n^{u}/(n^{u} - n^{t}) \\ &\quad + \Delta_f{}^{\circ}G_{B:A}[(n^{u})^{2} - 3n^{t}n^{u} + (n^{t})^{2}]/n^{t}(n^{u} - n^{t}) \qquad (27)\end{aligned}$$

$$\begin{aligned}{}^{\circ}L_{A,B:B} &= {}^{\circ}L_{A,B:A} \\ &\quad + (\Delta_f{}^{\circ}G_{B:A} - \Delta_f{}^{\circ}G_{A:B})(n^{u} - 2n^{t})/(n^{u} - n^{t}) \qquad (28)\end{aligned}$$

Without the °L parameters these equations can be simultaneously satisfied for $n^{t}=n^{u}$, only. The same conclusion was reached in Section 6 where n^{t} and n^{u} were denoted by P and Q. Such a case would be the B2→A2 transition. In order to predict an order–disorder transition for $n^{t}\neq n^{u}$, it is necessary to introduce all four regular solution parameters but only one of them may be regarded as an independent parameter, e.g. ${}^{\circ}L_{A,B:A}$. If it is assumed that the interactions within the second sublattice are independent of the occupancy of the first one, i.e. ${}^{\circ}L_{B:A,B}={}^{\circ}L_{A:A,B}$, then a combination of Eqs. (26) and (27) requires that $\Delta_f{}^{\circ}G_{B:A}=\Delta_f{}^{\circ}G_{A:B}$, and then Eq. (28) requires that ${}^{\circ}L_{A,B:A}={}^{\circ}L_{A,B:B}$. This yields

$$\begin{aligned}{}^{M}G_{m} &= [y^{t}_{A}y^{u}_{B}+y^{t}_{B}y^{u}_{A}+y^{u}_{A}y^{u}_{B}(n^{u}-n^{t})/n^{t}]\,\Delta_f{}^{\circ}G_{A:B}\\ &\quad+[y^{t}_{A}y^{t}_{B}+y^{u}_{A}y^{u}_{B}(n^{u}/n^{t})]\,{}^{\circ}L_{A,B:A}\\ &\quad+RT\sum\sum y^{s}_{J}\ln(y^{s}_{J}) \end{aligned} \tag{29}$$

Let us now compare with the bond energy model. If $n^{t}<n^{u}$, then it is natural to expect that there are no nearest neighbour bonds within the first sublattice and one may put ${}^{\circ}L_{A,B:A}$ and ${}^{\circ}L_{A,B:B}$ equal to zero. In that case the excess term that has been introduced in order to predict an order–disorder transition is $y^{u}_{A}y^{u}_{B}(n^{u}/n^{t}-1)\,\Delta_f{}^{\circ}G_{A:B}$. This is in complete agreement with Eq. (24) which was obtained by expressing the Bragg–Williams model in the compound energy formalism [15]. However, the compound energy model based on Eqs. (26)–(28) is less restrictive since it gives two extra degrees of freedom. First, one does not need to put $\Delta_f{}^{\circ}G_{B:A}$ and $\Delta_f{}^{\circ}G_{A:B}$ equal and, secondly, one has another degree of freedom when selecting the values of the independent regular solution parameter. In addition, one can introduce higher Redlich–Kister terms but only by obeying special constraints between them. Those constraints were studied by Ansara et al. [19] for the $L1_2$ structure.

8. Combination of mole fractions and site fractions

In Eq. (6) we used a combination of mole fractions and site fractions but that fact was later hidden by the introduction of the mixing Gibbs energy, ${}^{M}G_{m}$. In fact, it is used as soon as the Gibbs energy of formation of the compound, $\Delta_f{}^{\circ}G_{end}$, is used instead of the absolute value, ${}^{\circ}G_{end}$, which cannot be given a numerical value without the use of references. For ordered phases, which require the use of site fractions, Ansara et al. [19] proposed that it may sometimes be convenient to use the disordered state for the same composition as a kind of reference, expressed in terms of the mole fractions. The remaining part of the Gibbs energy could then be regarded as the contribution due to ordering and denoted by $\Delta G^{\text{ord.contr.}}$, not to be confused with the notation G^{ord}, which is sometimes used to represent the total Gibbs energy of the ordered state. The quantity $\Delta G^{\text{ord.contr.}}$ is expressed in terms of the site fractions. We shall now discuss this possibility for phases that occur in an ordered as well as a disordered state.

As shown by Eq. (6) the properties of a phase with two or more sublattices and without any complex constituents, i.e. with J identical to I, can be represented by an expression

$$\begin{aligned}{}^{M}G_{m}(y^{s}_{I}) &= \sum\Delta_f{}^{\circ}G_{end}\Pi y^{s}_{I}+RT\sum\sum n^{s}y^{s}_{I}\ln(y^{s}_{I})\\ &\quad+{}^{E}G_{m}(y^{s}_{I})\end{aligned} \tag{30}$$

This expression may be used for the description of an ordered phase. On the other hand, it may sometimes happen that an ordered phase can disorder at a sufficiently high temperature and the properties of the disordered state may even have been described before one turns the attention to the ordered state. One may then like to add a description that accounts for the change of properties caused by the ordering. The ordered state may appear at low temperatures, at different compositions or on adding an additional element. One would then like to retain the old description for the disordered state. Ansara et al. [19] argued that one should then redefine the expression for the mixing Gibbs energy per mole of formula units,

$${}^{M}G_{m}={}^{M}G^{\text{dis}}_{m}(x_{I})\cdot\sum n^{s}+\Delta G^{\text{ord.contr.}} \tag{31}$$

where ${}^{M}G^{\text{dis}}_{m}(x_{I})$ is the mixing Gibbs energy per mole of atoms in the disordered state and $\Delta G^{\text{ord.contr.}}$ represents the contribution due to ordering of the disordered state, counted per mole of formula units. It must vanish for the disordered state which can be accomplished by writing it as

$$\begin{aligned}\Delta G^{\text{ord.contr.}} &= {}^{M}G_{m}-{}^{M}G^{\text{dis}}_{m}(x_{I})\cdot\sum n^{s}\\ &=\Delta G^{\text{corr}}(y^{s}_{I})-\Delta G^{\text{corr}}(y^{s}_{I}=x_{I})\end{aligned} \tag{32}$$

where $\Delta G^{\text{corr}}(y^{s}_{I})$ is a function to be determined by optimizing the description of the ordering behaviour, based on the previous optimization of the disordered state. In Eq. (32) $\Delta G^{\text{ord.contr.}}$ has been treated as a function of y^{s}_{I} and x_{I} and the last term makes it vanish for the disordered state.

It is possible to eliminate the x_{I} variables using Eq. (4). For the case of no vacancies we have

$$x_{I}=\sum n^{s}y^{s}_{I}/\sum n^{s} \tag{33}$$

One would thus obtain

$$\Delta G^{\text{ord.contr.}}(y^{s}_{I})=\Delta G^{\text{corr}}(y^{s}_{I})-\Delta G^{\text{corr}}(y^{s}_{I}=\sum n^{s}y^{s}_{I}/\sum n^{s}) \tag{34}$$

and ${}^{M}G_{m}$ from Eq. (31) could be written as a function of only site fractions.

$$^{\mathrm{M}}G_{\mathrm{m}}(y_{\mathrm{I}}^{\mathrm{s}}) = \sum n^{\mathrm{s}} \cdot {}^{\mathrm{M}}G_{m}^{\mathrm{dis}}(x_{\mathrm{I}} = \sum n^{\mathrm{s}} y_{\mathrm{I}}^{\mathrm{s}} / \sum n^{\mathrm{s}}) + \Delta G^{\mathrm{corr}}(y_{\mathrm{I}}^{\mathrm{s}}) - \Delta G^{\mathrm{corr}}(y_{\mathrm{I}}^{\mathrm{s}} = \sum n^{\mathrm{s}} y_{\mathrm{I}}^{\mathrm{s}} / \sum n^{\mathrm{s}}) \quad (35)$$

It may look as if this function is not identical to $^{\mathrm{M}}G_{\mathrm{m}}(y_{\mathrm{I}}^{\mathrm{s}})$ given by Eq. (30) because they are based on different optimizations and, although one would hope that they both describe the real properties of $^{\mathrm{M}}G_{\mathrm{m}}$ well, they would not be identical because they are based on different sets of model parameters. However, as explained in Section 7, in order to make it possible for an ordered phase to disorder it is necessary to introduce relations between the model parameters, i.e. the parameters in Eq. (35). The sets of independent parameters may thus become identical for Eqs. (30) and (35).

It was recently pointed out by Sundman (B. Sundman, unpublished work) that it may also be advantageous to introduce a term depending on the composition and expressed in terms of the x_{I} variables even if the phase cannot disorder. He has proposed that this method should be called 'partitioning of the Gibbs energy'.

9. Model parameters and optimization parameters

Basically, the primary model parameters are the compound energies and their numerical values must be given relative to a set of standard states for the components, i.e. as Gibbs energy of formation. See Eq. (3). If the pure elements appear as end-members of the solution phase under consideration, then one can use those states as standard states but other choices may be more convenient or even necessary, in particular in calculations of equilibria between different phases where the same standard states must be used for all phases. In principle, it is permitted to choose any set of standard states.

When there are two or more sublattices, it may be convenient to introduce new model parameters instead of some of the compound energies. This can be illustrated with the simple reciprocal solution phase $(\mathrm{A,B})_1(\mathrm{D,E})_1$. Suppose the practical interest in a phase falls in the neighbourhood of the A:D end-member. It is then convenient to describe the various compositions using two independent site fractions, i.e. $y_{\mathrm{B}}^{\mathrm{t}}$ and $y_{\mathrm{E}}^{\mathrm{u}}$, and eliminate the other two by inserting $y_{\mathrm{A}}^{\mathrm{t}} = 1 - y_{\mathrm{B}}^{\mathrm{t}}$ and $y_{\mathrm{D}}^{\mathrm{u}} = 1 - y_{\mathrm{E}}^{\mathrm{u}}$. One then obtains

$$\begin{aligned} ^{\mathrm{M}}G_{\mathrm{m}} = {} & \Delta_f{}^{\circ}G_{\mathrm{A:D}} + y_{\mathrm{B}}^{\mathrm{t}}(\Delta_f{}^{\circ}G_{\mathrm{B:D}} - \Delta_f{}^{\circ}G_{\mathrm{A:D}}) \\ & + y_{\mathrm{E}}^{\mathrm{u}}(\Delta_f{}^{\circ}G_{\mathrm{A:E}} - \Delta_f{}^{\circ}G_{\mathrm{A:D}}) \\ & - y_{\mathrm{B}}^{\mathrm{t}} y_{\mathrm{E}}^{\mathrm{u}}({}^{\circ}G_{\mathrm{A:E}} + {}^{\circ}G_{\mathrm{B:D}} - {}^{\circ}G_{\mathrm{A:D}} - {}^{\circ}G_{\mathrm{B:E}}) \\ & + RT \sum \sum y_{\mathrm{I}}^{\mathrm{s}} \ln(y_{\mathrm{I}}^{\mathrm{s}}) + {}^{\mathrm{E}}G_{\mathrm{m}} \end{aligned} \quad (36)$$

The first three terms are defined by the three compound energies $\Delta_f{}^{\circ}G_{\mathrm{A:E}}$, $\Delta_f{}^{\circ}G_{\mathrm{A:D}}$ and $\Delta_f{}^{\circ}G_{\mathrm{B:D}}$. For dilute solutions one can neglect the fourth term because $y_{\mathrm{B}}^{\mathrm{t}}$ and $y_{\mathrm{E}}^{\mathrm{u}}$ are both small but for richer solutions it represents a deviation from ideal solution behaviour. The coefficient $({}^{\circ}G_{\mathrm{A:E}} + {}^{\circ}G_{\mathrm{B:D}} - {}^{\circ}G_{\mathrm{A:D}} - {}^{\circ}G_{\mathrm{B:E}})$ was already defined by Eq. (7), using the notation $\Delta{}^{\circ}G_{\mathrm{A,B:D,E}}$ and it represents the standard Gibbs energy of the reciprocal reaction A:E + B:D→A:D + B:E and was called 'reaction parameter'. It would be more meaningful to give that parameter than the fourth compound energy, $\Delta_f{}^{\circ}G_{\mathrm{B:E}}$. An important characteristic of the reaction parameter is that its numerical value is independent of the choice of standard states. It thus describes properties of the phase itself. For example, it was already mentioned in Section 3 that this parameter directly controls the tendency of demixing and in Section 6 that it controls the tendency of ordering if there are no excess terms. As a consequence, it is convenient to work with the reaction parameter when optimizing the description of a phase. One can often make a reasonable first guess of its value, one can foresee the effect of a change in its value during an optimization and one can predict when it will have a negligible influence on the properties and would not need to be optimized. It is thus strongly recommended that reaction parameters should be used as 'optimization parameters' in addition to those compound energies that are needed to describe dilute solutions.

When there are more than two sublattices and more than two constituents on each one, there may be a large number of reciprocal subsystems but all their reaction parameters cannot be included in the set of optimization parameters because all of them are not independent. It is necessary to select some of them as the independent ones and include only those in the set of optimization parameters [20]. As an example, with two sublattices with m and n constituents, respectively, there will be $m \cdot n$ end-member compounds and $m \cdot n$ optimization parameters are needed. One of the compounds may be regarded as the main one and dilute solutions in that compound may be described by adding the energies of all the compounds obtained by substituting one at a time of the remaining constituents. We have thus selected $1 + (m-1) + (n-1)$ optimizing parameters and need $m \cdot n - [1 + (m-1) + (n-1)] = (m-1) \cdot (n-1)$ more. They should come from the reaction parameters but their total number is $(m-1)! \cdot (n-1)!$ which may be much larger.

The strategy for selecting the independent reaction parameters could be as follows. For each sublattice, arrange the constituents in their order of importance judged by the maximum value of their site fractions. The compounds used to define the model in the compound energy formalism are obtained by taking one constituent for each sublattice. The main compound is defined by taking the first one for each sublattice. The compounds to be used in the dilute solution approximation are defined by instead including one at a time of the remaining constituents. For all these compounds $\Delta_f{}^{\circ}G_{\mathrm{end}}$ will be included in the set of optimization parameters. Then, define a compound by selecting the second constituent in two of the sublattices, and express its compound energy using the reciprocal system with compounds already selected. This procedure can be continued to include less and less important constituents until all compounds have been covered. For example, suppose the constituents are already arranged according to their importance in the formula $(\mathrm{A,B,C})_k(\mathrm{D,E,F})_l(\mathrm{G,H,I})_m$. First include $\Delta_f{}^\circ G_{\mathrm{A:D:G}}$ in the set of optimization parameters in order to represent the major constituents, and then $\Delta_f{}^\circ G_{\mathrm{B:D:G}}$, $\Delta_f{}^\circ G_{\mathrm{A:E:G}}$, $\Delta_f{}^\circ G_{\mathrm{A:D:H}}$, $\Delta_f{}^\circ G_{\mathrm{C:D:G}}$, $\Delta_f{}^\circ G_{\mathrm{A:F:G}}$ and $\Delta_f{}^\circ G_{\mathrm{A:D:I}}$ to represent the minor constituents. Then, define

$$\Delta_f{}^\circ G_{\mathrm{B:E:G}} = \Delta_f{}^\circ G_{\mathrm{A:E:G}} + \Delta_f{}^\circ G_{\mathrm{B:D:G}} - \Delta_f{}^\circ G_{\mathrm{A:D:G}} - \Delta^\circ G_{\mathrm{A,B:D,E:G}} \tag{37}$$

and include $\Delta^\circ G_{\mathrm{A,B:D,E:G}}$ in the set. Next, define

$$\Delta_f{}^\circ G_{\mathrm{B:D:H}} = \Delta_f{}^\circ G_{\mathrm{A:D:H}} + \Delta_f{}^\circ G_{\mathrm{B:D:G}} - \Delta_f{}^\circ G_{\mathrm{A:D:G}} - \Delta^\circ G_{\mathrm{A,B:D:G,H}} \tag{38}$$

and include $\Delta^\circ G_{\mathrm{A,B:D:G,H}}$ in the set, etc. The last compound would be CFI and its energy could be defined using

$$\Delta_f{}^\circ G_{\mathrm{C:F:I}} = \Delta_f{}^\circ G_{\mathrm{A:F:I}} + \Delta_f{}^\circ G_{\mathrm{C:D:I}} - \Delta_f{}^\circ G_{\mathrm{A:D:I}} - \Delta^\circ G_{\mathrm{A,C:D,F:I}} \tag{39}$$

since $\Delta_f{}^\circ G_{\mathrm{A:F:L}}$, $\Delta_f{}^\circ G_{\mathrm{C:D:I}}$ and $\Delta_f{}^\circ G_{\mathrm{A:D:I}}$ have been defined earlier in the process and their definitions can be inserted. All the compound energies have thus been defined in terms of the new set of optimizing parameters which does not include all possible reaction parameters.

It may often happen that the available experimental information is not sufficient for a meaningful optimization of all the optimization parameters. It may then be necessary to use theoretical or empirical methods of estimating the values of some of them and not let them vary during the optimization. This method should primarily be applied at the end of the list of parameters. Often the importance of a reaction parameter at the end of the list could even be so small that any value, e.g. zero, could be used. For a complicated phase with a very large number of end-member compounds it may be convenient to put many of the independent reaction parameters to zero.

Of course, excess terms with regular or Redlich–Kister parameters should be used only for reciprocal systems at the beginning of the list of reciprocal systems and only when there is sufficient experimental information to determine them.

10. Ionic crystals

If the constituents are ions, it is possible that the compound energy model uses some end-members that are not neutral. An example would be the solution of NaCl in $\mathrm{CaCl_2}$. It may be described with the formula $(\mathrm{Ca^{+2},Na^{+1}})_1(\mathrm{Cl^{-1},Va^0})_2$, yielding a diagram somewhat resembling that for $(\mathrm{A,B})_1(\mathrm{B,Va})_1$ in Fig. 2. However, $\mathrm{CaCl_2}$ would be the only neutral end-member. Instead of lines for constant composition one now obtains lines for constant charge, one of which being the neutral line. It would start from the $\mathrm{CaCl_2}$ corner and have a slope of 1/2. Only compositions on the neutral line would be of practical interest but the model describes the whole square which may thus be regarded as a true composition square. When making calculations one must add the condition of electroneutrality. This is done automatically by existing software.

The same phenomenon occurs without the action of vacancies if there are two sublattices for the cations and they have different valancies, an example being the spinel phase. It is a double oxide with a divalent and a trivalent metal. In a normal spinel they prefer different sublattices and the ideal structure would normally be $(\mathrm{A^{+2}})_1(\mathrm{E^{+3}})_2(\mathrm{O^{-2}})_4$. However, the cations can go into anti-site positions, yielding $(\mathrm{A^{+2},E^{+3}})_1(\mathrm{E^{+3},A^{+2}})_2(\mathrm{O^{-2}})_4$. The constitution can thus vary but only along a neutral line in the square. See Fig. 4. It should be noticed that in this case the neutral line represents a single composition $\mathrm{AO\cdot E_2O_3}$ and the state of equilibrium is obtained by minimizing the Gibbs energy under the condition of electroneutrality or constant composition corresponding to $\mathrm{AO\cdot E_2O_3}$.

The right-hand end-point on the neutral line in Fig. 4 represents so-called ‘inverse spinel’, $(\mathrm{E^{+3}})_1(\mathrm{E^{+3}_{0.5},A^{+2}_{0.5}})_2(\mathrm{O^{-2}})_4$ and in some systems it is more stable than the ‘normal spinel’. If one adds a second trivalent metal, the formula would be $(\mathrm{A^{+2},E^{+3},F^{+3}})_1(\mathrm{E^{+3},F^{+3},A^{+2}})_2(\mathrm{O^{-2}})_4$ and the composition can vary but only with respect to the relative contents

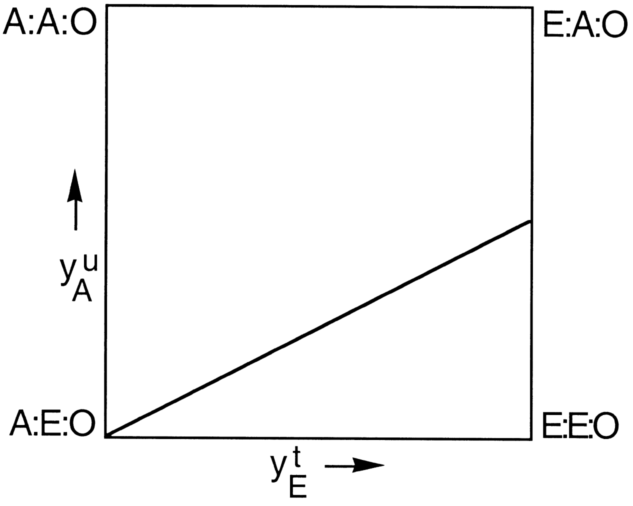

Fig. 4. The so-called composition square for a spinel phase $(\mathrm{A^{+2},E^{+3}})_1(\mathrm{E^{+3},A^{+2}})_2(\mathrm{O^{-2}})_4$. The straight line represents possible constitutions for the only composition allowed by the electroneutrality requirement. Three of the corners represent hypothetical compounds that are charged. In the compound energy formalism they only appear in neutral combinations.

of E_2O_3 and F_2O_3. One may use $(y^{t}_{E}-y^{t}_{F})/4+(y^{u}_{E}-y^{u}_{F})/2$ as a composition variable which could vary from 0.5 to -0.5. By combination with the y^{t}_{A} and y^{u}_{A} variables from Fig. 4 (after replacing y^{t}_{E} by $1-y^{t}_{A}$) we now obtain a three-dimensional diagram with a neutral plane. If a fourth metal is added, there will be a four-dimensional diagram which could not be illustrated graphically [21].

In the mathematical model of crystalline ionic phases there will appear the Gibbs energy of formation of the charged compounds represented by all the non-neutral end-members. It does not make sense to try to give them realistic numerical values because they only appear in neutral combinations when the condition of electroneutrality is applied during calculations. Thus, one of them is selected as a reference and the other ones are given through neutral combinations with this one. In the last example, one may select $(E^{+3})_1(E^{+3})_2(O^{-2})_4$ with one positive charge as a reference and quite arbitrarily define $\Delta_f{}^{\circ}G_{E:E}=0$. (For simplicity we shall here omit O from the subscript.) Then one can give numerical values to the others, e.g. $(E^{+3})_1(A^{+2})_2(O^{-2})_4$, but it may be wise to remember that the value of $\Delta_f{}^{\circ}G_{E:A}$ actually holds for $\Delta_f{}^{\circ}G_{E:A}+\Delta_f{}^{\circ}G_{E:E}$ which represents the value of a neutral combination since $(E^{+3})_1(A^{+2})_2(O^{-2})_4$ has a negative charge that compensates for the positive charge of $(E^{+3})_1(E^{+3})_2(O^{-2})_4$.

As an example, consider a simple spinel $(A^{+2},E^{+3})_1(E^{+3},A^{+2})_2(O^{-2})_4$. Experimentally one would only be able to study a single point in the whole reciprocal system, the point on the neutral line that represents the stable constitution. One could hope to measure its Gibbs energy and composition. Thus, it would normally be possible to evaluate two parameters, only, whereas the compound energy formalism description would contain eight parameters if the regular solution parameters $L_{A:A,E}$, $L_{E:A,E}$, $L_{A,E:A}$ and $L_{A,E:E}$ are all included. However, one could simply put $\Delta^{\circ}G_{A,E:E,A}$ and all the L parameters to zero. Then, putting $\Delta_f{}^{\circ}G_{E:E}$ to zero as a choice of reference for charges one could work with $\Delta_f{}^{\circ}G_{A:E}$ and $\Delta_f{}^{\circ}G_{E:A}$ as the only optimization parameters and insert $\Delta_f{}^{\circ}G_{A:E}+\Delta_f{}^{\circ}G_{E:A}$ instead of $\Delta_f{}^{\circ}G_{A:A}$.

As one builds up a database for a phase, covering many elements, there will be many subsystems and initially one may select a reference for charges in each one. However, in order to combine the descriptions of two subsystems it is necessary to have the same reference for charges and it will soon be necessary to accept a description of a subsystem with a reference that is not part of the subsystem itself. This is a well-known situation from aqueous solutions where there is international agreement to use a reference defined by the use of the hydrogen ion. It is evident that one should try to reach international agreement on the reference to be used for each one of all the ionic phases of general interest. However, it will take a long time until enough systems have been assessed to justify such an effort.

In order to introduce a common reference for charges in two subsets it is necessary to have information from a combined system which can be used to relate the two initial references to each other. If there are two such combined systems, and they are used for this purpose on different occasions, different relations may be obtained which will cause an inconsistency in the combined dataset. Thus, the relation should only be derived on one occasion, and preferably under the use of all possible information in one optimization procedure.

For each kind of phase one will ultimately be able to introduce a single reference for charges but during the development of various subsets one may be forced to use different references. In order to avoid incorrect combinations one should store each subset under a separate phase name as long as it is described with its own reference for charges. It is also essential to show clearly in the dataset what reference for charges has been used.

If the oxide contains vacancies, there may be experimental information on the composition as a function of the oxygen potential. For example, consider the cerium dioxide which can show a strong deviation from stoichiometry. One could write its formula as $(Ce^{+4},Ce^{+3})_1(O^{-2},Va^{0})_2$. The reaction with oxygen can be written as

$$4Ce^{+4}+2O^{-2}=4Ce^{+3}+O_2 \tag{40}$$

However, in order to use the compound energy formalism we like to introduce the end-members and it has been shown [22] that this can be done by replacing Ce^{+4} with $(Ce^{+4})_1(O^{-2})_2$ and Ce^{+3} with $(Ce^{+3})_1(O^{-2})_2$ and, finally, $2O^{-2}$ with $(Ce^{+4})_1(O^{-2})_2$–$(Ce^{+4})_1(Va^{0})_2$ obtaining

$$5(Ce^{+4})_1(O^{-2})_2=(Ce^{+4})_1(Va^{0})_2+4(Ce^{+3})_1(O^{-2})_2+O_2 \tag{41}$$

We would thus obtain

$$2\mu_{O}=5G_{Ce^{+4}O_2}-G_{Ce^{+4}Va_2}-4G_{Ce^{+3}O_2} \tag{42}$$

and can obtain μ_O by calculating the three partial Gibbs energies from Eq. (11). The result can then be compared with the experimental information in the optimization procedure. It is important to notice that with modern software one can calculate μ_O directly without deriving an expression like Eq. (42).

11. Point defects in semiconductors

Binary semiconductors with the zinc blende structure have two sublattices. They are crystallographically equivalent but are mainly occupied by one component each. Anti-site atoms are the most common point defects but there are also ionized atoms in addition to free electrons and holes. When modelling this type of phase one must decide where to put the electrons and holes. When modelling the Ga–As system Chen and Hillert [20] argued that they should not be put in any of the two sublattices for atoms and instead they were put each one in its own sublattice. That had the advantage that the number of sites on those sublattices could be chosen as N_C and N_V, the effective number of sites for electrons and holes, respectively, at their energy levels. They can be estimated from the effective masses of electrons at the conduction band edge and of holes at the valence band edge, respectively [23]. However, this method would make the modelling very complicated if N_C and N_V vary with composition, which would certainly happen in higher order systems. Thus it was finally recommended to make the number of sites equal in all the sublattices and compensate for the incorrect number of sites for the electrons and holes by subtracting the terms $RT\ln(N_C)$ and $RT\ln(N_V)$ from their Gibbs energy of formation, which would yield practically the same result as long as the number of electrons and holes are much less than N_C and N_V, respectively. It is then possible to use the compound energy formalism and allow N_C and N_V to vary with composition if more elements are added. It should further be mentioned that the sum of the Gibbs energy of formation for electrons and holes was taken from the width of the band gap. The model was thus defined as

$$(\mathbf{A},\mathrm{B},\mathrm{B}^{+})_1(\mathbf{B},\mathrm{A},\mathrm{A}^{-})_1(\mathbf{Va},\mathrm{e}^{-})_1(\mathbf{Va},\mathrm{h}^{+})_1$$

where part of the anti-site atoms were assumed singly ionized, and thus become native donors or acceptors. The model based on this formula was treated directly with the Thermo-Calc program.

In a subsequent study of the Cd–Te system [23], vacancies and interstitials of Cd were also considered and a model defined by the formula

$$(\mathbf{Cd},\mathrm{Va},\mathrm{Va}^{-2},\mathrm{Te})_1(\mathbf{Te},\mathrm{Va},\mathrm{Va}^{+2},\mathrm{Cd})_1(\mathbf{Va},\mathrm{Cd},\mathrm{Cd}^{+2})_1(\mathbf{Va},\mathrm{e}^{-})_1\text{-}(\mathbf{Va},\mathrm{h}^{+})_1$$

was used. According to this model, interstitial Cd (in third sublattice where vacancies make the major constituent) acts as a native donor in Cd rich material and vacancies on the Cd sublattice act as native donors in Te rich material. Neutral anti-sites are assumed on both main sublattices in order to account for the relatively large homogeneity range of the CdTe phase. The choice of divalency for defects in this system is recommended in view of previous examinations of the variation of electrical properties with composition and was also supported by the results of the new assessment. It is interesting to note that even this case with five sublattices could be treated directly with the Thermo-Calc program. The strategy to define the optimization parameters, outlined in Section 9, was used in that study.

12. Ionic melts

When developing a regular solution model for ionic melts, Hillert and Staffansson [6] accepted a proposal by Temkin [24] that the structure could be approximated by two sublattices, one each for cations and anions. This proposal had been further developed by Flood, Förland and Grjotheim [25]. Hillert and Staffansson discussed how to define a non-planar surface of reference and they proposed an expression similar to Eq. (2) but with site fractions based on equivalents instead of atoms and denoted z_J. For crystalline phases they replaced z_J with the ordinary site fraction y_J. For crystalline phases the model was extended to many components and sublattices by Harvig [7] and Sundman and Ågren [8].

When later trying to apply the model to melts with variable tendency for ionization, Hillert, Jansson, Sundman and Ågren [26] found it more convenient to use the ordinary site fractions in that case as well. They could then introduce neutral species on the anion sublattice which allowed the model to cover compositions all the way to the non-metallic side. They discussed the corresponding method for extending the description all the way to the metallic side but finally decided instead to recommend the introduction of hypothetical vacancies in the anion sublattice with a valency equal to the average valency on the cation sublattice, but with a negative sign. The Cu–S melt was thus modelled with the formula $(\mathrm{Cu}^{+1})_P(\mathrm{S}^{-2},\mathrm{Va}^{-1},\mathrm{S}^{0})_Q$. (It should be noted that the Thermo-Calc software requires that neutral constituents are placed last in the ionic liquid model.) In order to satisfy electroneutrality it was necessary to let the stoichiometric coefficients vary with composition in the following controlled way,

$$Q=\sum \nu_c y_c = -\nu_{Va} \tag{43}$$

$$\begin{aligned}P &= -\sum \nu_a y_a - \nu_{Va} y_{Va} = -\sum \nu_a y_a + y_{Va}\sum \nu_c y_c \\ &= -\sum \nu_a y_a + Q y_{Va}\end{aligned} \tag{44}$$

where the cations are denoted by the subscript c and the anions by a. When applying Eq. (2) the terms with neutral species, denoted by n, may be written as

$$\sum\sum y_c y_n {}^\circ G_{c:n} = \sum \nu_c y_c \sum y_n {}^\circ G_n = Q\sum y_n {}^\circ G_n \tag{45}$$

because an end-member with a neutral constituent would be $c_0 n_{\nu_c}$, i.e. ν_c atoms of n. The quantity ${}^\circ G_n$ is here defined for one mole of atoms of n. An end-member with vacancies would have the following formula unit according to Eq. (43),

$$\begin{aligned}(c^{\nu_c})_P(\mathrm{Va}^{\nu_{Va}})_Q &= (c^{\nu_c})_Q(\mathrm{Va}^{-Q})_Q = (c^{\nu_c})_{\nu_c}(\mathrm{Va}^{-\nu_c})_{\nu_c} \\ &= \nu_c(c^{\nu_c})_1(\mathrm{Va}^{-\nu_c})_1\end{aligned} \tag{46}$$

This would be identical to ν_c neutral atoms of c. However, we shall soon see that we must define the end-member of the cation c with vacancies as Q neutral atoms of c instead of ν_c. The full expression obtained from Eq. (6) will thus be

$$
\begin{aligned}
{}^{M}G_m = {} & \sum\sum y_c y_a \Delta_f{}^\circ G_{c:a} + Q y_{Va} \sum y_c\, \Delta_f{}^\circ G_c \\
& + Q \sum y_n\, \Delta_f{}^\circ G_n + RT[P \sum y_c \ln(y_c) \\
& + Q \sum y_j \ln(y_j)] + {}^{E}G_m \qquad (47)
\end{aligned}
$$

where ${}^\circ G_c$ is a quantity defined for one mole of atoms of c. It should be noted that this modification does not affect the total content of cations because $Q y_{Va} \cdot \Sigma y_c$ is equal to $\Sigma \nu_c y_c y_{Va} \cdot 1$. The subscript j represents all species on the anion sublattice, i.e. anions, neutral species and vacancies. $\Delta_f{}^\circ G_c$ and $\Delta_f{}^\circ G_n$ are the differences between the liquid states of one mole of pure c or n at the actual temperature and in the reference states. It should be remembered that $\Delta_f{}^\circ G_c$ formally contains also one mole of vacancies.

The amount of each cation, c, per mole of formula units will be $y_c \Sigma y_a(-\nu_a) + Q y_{Va} y_c + 0$ according to Eq. (47), which is equal to $P y_c$ according to Eq. (44). This is the correct value and that is why the end-member of cation c with vacancies was defined as Q neutral atoms of c. The amount of each anion is $y_a \Sigma y_c \nu_c = Q y_a$ which is also a correct value. The amount of each neutral constituent is $Q y_n$, again a correct value.

Sundman [27] has discussed the excess terms. They should reduce to the ordinary ones on a binary metallic side, $y_A y_B L_{A,B}$. This will be the case if $L_{A,B:Va} = Q L_{A,B}$. With $y_{Va} = 1$ and $y_a = y_n = 0$ Eq. (47) would reduce to

$$
\begin{aligned}
{}^{M}G_m &= Q y_{Va}(y_A\, \Delta_f{}^\circ G_A + y_B\, \Delta_f{}^\circ G_B) + PRT[y_A \ln(y_A) \\
&\quad + y_B \ln(y_B)] + y_A y_B y_{Va} L_{A,B:Va} \\
&= Q[x_A\, \Delta_f{}^\circ G_A + x_B\, \Delta_f{}^\circ G_B + RT[x_A \ln(x_A) \\
&\quad + x_B \ln(x_B)] + x_A x_B L_{A,B}] \qquad (48)
\end{aligned}
$$

because here $P = Q$ according to Eq. (44). This expression for ${}^{M}G_m$ thus refers to Q moles of atoms.

The excess terms should also reduce to the ordinary ones on a binary non-metallic side, $y_D y_E L_{D,E}$, where D and E are two neutral species. This will be the case if $L_{A:D,E} = \nu_A L_{D,E}$ and $L_{B:D,E} = \nu_B L_{D,E}$. With only neutral species on the anion sublattice, $y_a = y_{Va} = 0$ and $P = 0$ according to Eq. (34) and Eq. (47) would reduce to

$$
\begin{aligned}
{}^{M}G_m &= Q(y_D\, \Delta_f{}^\circ G_D + y_E\, \Delta_f{}^\circ G_E) \\
&\quad + QRT[y_D \ln(y_D) + y_E \ln(y_E)] \\
&\quad + (y_A \nu_A + y_B \nu_B) y_D y_E L_{D,E} \\
&= Q[x_D\, \Delta_f{}^\circ G_D + x_E\, \Delta_f{}^\circ G_E + RT[x_D \ln(x_D) \\
&\quad + x_E \ln(x_E)] + x_D x_E L_{D,E}] \qquad (49)
\end{aligned}
$$

Again, we obtain an expression for Q moles of atoms. It should be added that, in addition to $L_{A:D,E}/\nu_A = L_{B:D,E}/\nu_B = L_{D,E}$, one must put the reciprocal parameter to zero, $L_{A,B:D,E} = 0$.

This model is very flexible but it should be noticed that it does not primarily consider the interaction between two neutral species or two cations through the compound energies because they are treated as not being neighbours since they are assumed to reside in the same sublattice. However, this can hardly be realistic when the contents of ions decrease to low values and the cation sublattice is disappearing. In order to describe such effects it is necessary to use interaction terms through the excess Gibbs energy in Eqs. (48) and (49).

For a molten mixture of salts there will be no neutral constituents or vacancies and one may take $(\mathrm{Na}^{+1},\mathrm{Ca}^{+2})_P(\mathrm{Cl}^{-1},\mathrm{SO}_4^{-2})_Q$ as an example. On the other hand, there are molten salts that can dissolve an excess of metal. As an example, the Ca–CaF$_2$ liquid can be modelled with the formula $(\mathrm{Ca}^{+2})_P(\mathrm{F}^{-1},\mathrm{Va}^{-2})_2$ and even with $(\mathrm{Ca}^{+2})_P(\mathrm{F}^{-1},\mathrm{Va}^{-2},\mathrm{F}^0)_2$ if one also likes to describe an excess of F [28].

The molten solution between an orthosilicate and its component metal is modelled as $(\mathrm{Ca}^{+2})_P(\mathrm{O}^{-2},\mathrm{SiO}_4^{-4},\mathrm{Va}^{-2})_2$. At higher SiO$_2$ contents there will appear more complex silica species and pure molten SiO$_2$ may be regarded as a single, huge molecule, held together by covalent bonds. As an approximation, simple enough to be handled, all such complex situations are handled by the introduction of a hypothetical, neutral species, SiO_2^0 [29]. For the above case, the complete model will thus be $(\mathrm{Ca}^{+2})_P(\mathrm{O}^{-2},\mathrm{SiO}_4^{-4},\mathrm{Va}^{-2},\mathrm{SiO}_2^0)_2$ and it covers the whole composition range in the triangle Ca–CaO–SiO$_2$. In Al$_2$O$_3$ the bonding has a considerable covalent character and the Al$_2$O$_3$–SiO$_2$ liquid has been modelled simply as $(\mathrm{Al}_1\mathrm{O}_{1.5}^0, \mathrm{SiO}_2^0)$ [30]. Following that suggestion, the CaO–Al$_2$O$_3$ liquid was modelled as $(\mathrm{Ca}^{+2},\mathrm{Al}^{+3})_P(\mathrm{O}^{-2},\mathrm{Al}_1\mathrm{O}_{1.5}^0)_Q$ and Fe$_2$O$_3$ was represented by the species FeO$_{1.5}$, e.g. in the Fe–O system where the formula $(\mathrm{Fe}^{+2})_P(\mathrm{O}^{-2},\mathrm{Va}^{-2},\mathrm{Fe}_1\mathrm{O}_{1.5}^0)_2$ was used [31].

13. Short range order in crystals

In reality the atoms may not be distributed at random within their sublattices but be influenced by interactions with other atoms. One talks about short range order. To describe such a situation one needs more independent variables than there are independent mole or site fractions. This problem was first treated by Bethe [10] who considered the probabilities for bonds between nearest neighbour atoms. In a disordered alloy one could work with three pair probabilities, p_{AA}, p_{AB} and p_{BB}, two of which are independent which is one more than the only independent mole fraction. In an alloy with long range order over two sublattices in a structure, where all nearest neighbour bonds fall between the sublattices, one would have to distinguish between $p_{A:B}$ and $p_{B:A}$. This addition of another pair probability makes it possible to describe both long and short range order. The energy is obtained by summation over the bond energies and the configurational entropy is obtained by considering the mixing of the bonds, using a statistical treatment today often called the quasi-chemical approximation. Kikuchi [32] developed this model further by considering larger groups of atoms and several sizes at the same time in the so-called cluster variation method (CVM).

The compound energy formalism is basically a random mixing model but can be extended to include short range order by using the quasi-chemical approximation or some of the features of CVM. The logical way to introduce short range order into a compound energy model would be to consider the entities defined by the compounds (end-members) already used in the random mixing model. One would thus modify Eq. (2) by introducing the probabilities for atomic arrangements corresponding to the end-members, p_{end}.

$$G_m^{s.r.} = \sum p_{end} {}^{\circ}G_{end} \tag{50}$$

The basic part of the entropy of mixing now comes from the mixing of these groups of atoms

$$S_m^{mix} = -zR \sum p_{end} \ln(p_{end}) \tag{51}$$

where z is the number of such groups per mole of formula units. However, this expression overestimates the entropy. There are restrictions on the mutual arrangements of the groups and one should at least require that the ordinary expression for random mixing of atoms is recovered when the probabilities take the values for random mixing, i.e. when $p_{end} = \Pi y_J^s$. Following the quasi-chemical approach, as derived by Guggenheim [33] for a case with two sublattices and all the nearest neighbour bonds falling between the sublattices, Sundman [34] wrote

$$S_m^{mix} = -zR \sum p_{end} \ln(p_{end}/\Pi y_J^s) - R \sum\sum n^s y_J^s \ln(y_J^s) \tag{52}$$

The terms in the first summation will drop out for random mixing, leaving the second summation which is the well-known expression for random mixing within each sublattice. For two sublattices one would have the four variables $p_{A:A}$, $p_{A:B}$, $p_{B:A}$ and $p_{B:B}$, and their values at random mixing would be $y_A^t y_A^u$, $y_A^t y_B^u$, $y_B^t y_A^u$ and $y_B^t y_B^u$, respectively. This compound energy model would be identical to the corresponding quasi-chemical treatment. It remains to be discussed whether the p_{end} variables should also be introduced into the excess terms of Eq. (5). When considering a two-sublattice model for ionic melts, Dessureault and Pelton [35] considered the case of two sublattices with two ions on each and all ions of the same valency, $(A,B)_1(X,Y)_1$. They wrote the factor $y_A y_B y_X$ in an excess term as $(y_A y_X)(y_B y_X)/y_X$ and modified it to an expression equivalent to $p_{A:X} p_{B:X}/y_X$. An alternative would be to write this factor as $(y_A y_B y_X + y_B y_A y_X)/2$ and modify it to $(y_A p_{B:X} + y_B p_{A:X})/2$ which may be simpler to handle in calculations.

In an actual calculation one must determine the distribution over the various sublattices (i.e. long range order) and the non-random distribution within the sublattices (i.e. short range order) by minimizing G_m with respect to all the p_{end} variables under constant composition. Thus, all the p_{end} variables will be fixed and together they will represent long and short range order. In such a calculation it is necessary to express the site fractions appearing in Eq. (52) in terms of the probabilities, which is easily done. For two sublattices one gets relations like

$$y_A^t = p_{A:A} + p_{A:B} \tag{53}$$

Alternatively, one could work directly with site fractions but then one must also introduce variables representing short range order. For the simple case discussed here, Sundman [34] replaced the first set of variables with the second one using

$$p_{A:A} = y_A^t y_A^u - \varepsilon \tag{54}$$

$$p_{A:A} = y_A^t y_B^u + \varepsilon \tag{55}$$

$$p_{A:A} = y_B^t y_A^u + \varepsilon \tag{56}$$

$$p_{A:A} = y_B^t y_B^u - \varepsilon \tag{57}$$

The short range order variable ε is here defined as

$$\varepsilon = p_{A:B} p_{B:A} - p_{A:A} p_{B:B} \tag{58}$$

For a more complex system such relations will be more complicated, in particular when there are more than one degree of freedom for short range order. It thus seems that a general program for such calculations should be based directly on the p_{end} variables. Such a program is not yet available.

In order to make all nearest neighbour bonds fall between sublattices it would be necessary to define four sublattices for the f.c.c. structure A1. For a binar alloy there would then be 16 p_{end} variables, $p_{A:A:A:A}$, $p_{A:A:A:B}$, $p_{A:A:B:A}$ and $p_{A:B:A:A}$, etc. If the corresponding groups of four atoms are regarded as tetrahedra, then one could improve the entropy expression, Eq. (52), by using a result from CVM which also includes a contribution from the mixing of pairs. This was done by Sundman and Mohri [16] and they expressed the compound energies by relating them to the bond energies for pairs. Their calculations were rather complicated because of the large number of variables. It could be simplified if one would only be interested in a certain type of long range order, e.g. the $L1_2$ structure. However, in order to treat alloys with more elements it is desirable to simplify the treatment further and such an attempt was made by Sundman [34].

Following a proposal by Blander and Yosim [36] for ionic melts, Sundman et al. [17] recently suggested that one could add the reciprocal term, $y_{\mathrm{A}}^{\mathrm{t}}y_{\mathrm{B}}^{\mathrm{t}}y_{\mathrm{A}}^{\mathrm{u}}y_{\mathrm{B}}^{\mathrm{u}}L_{\mathrm{A,B:A,B}}$, as an approximate description of the effect of short range order in crystalline phases with two sublattices. Thus, one would avoid the necessity of evaluating the effect of short range order from the minimization of the Gibbs energy. For the Au–Cu system they considered four sublattices and introduced reciprocal terms of the form $y_{\mathrm{A}}^{\mathrm{t}}y_{\mathrm{B}}^{\mathrm{t}}y_{\mathrm{A}}^{\mathrm{u}}y_{\mathrm{B}}^{\mathrm{u}}y_{\mathrm{A}}^{\mathrm{v}}y_{\mathrm{A}}^{\mathrm{w}}L_{\mathrm{A,B:A,B:A:A}}$.

14. Short range order in ionic melts

Dessureault and Pelton [35] have treated short range order in ionic melts when the cations have equal valencies and also the anions. In that case the stoichiometric coefficients, defined by Eqs. (43) and (44), have constant values and the treatment for crystals can be applied directly to a melt. Selleby and Sundman (M. Selleby and B. Sundman, personal communication) have recently shown how a short range order treatment can be developed from the compound energy formalism for cases with a mixture of valancies, even including neutral species, and with vacancies. Before discussing their method a related treatment based directly on Eq. (47) for random melts will be presented. The same type of probabilities p_{end} as before will be introduced in Eq. (47).

$$\begin{aligned}{}^{\mathrm{M}}G_{\mathrm{m}} = {} & \sum\sum p_{\mathrm{c:a}}\,\Delta_f{}^{\circ}G_{\mathrm{c:a}} + Q\sum p_{\mathrm{c:Va}}\,\Delta_f{}^{\circ}G_{\mathrm{c}} \\ & + Q\sum p_{\mathrm{n}}\,\Delta_f{}^{\circ}G_{\mathrm{n}} \\ & + zRT\Big[\sum\sum p_{\mathrm{c:a}}\ln(p_{\mathrm{c:a}}/y_{\mathrm{c}}y_{\mathrm{a}}) \\ & + \sum p_{\mathrm{c:Va}}\ln(p_{\mathrm{c:Va}}/y_{\mathrm{c}}y_{\mathrm{Va}}) + \sum p_{\mathrm{n}}\ln(p_{\mathrm{n}}/y_{\mathrm{n}})\Big] \\ & + RT\Big[P\sum y_{\mathrm{c}}\ln(y_{\mathrm{c}}) + Q\sum y_{\mathrm{j}}\ln(y_{\mathrm{j}})\Big] + {}^{\mathrm{E}}G_{\mathrm{m}} \qquad (59)\end{aligned}$$

It should be remembered that the subscript j represents all species in the anion sublattice whereas the subscript a only represents the true anions. The number of bonds per formula unit, z, is not well defined in this case. A formula unit contains $P + Q$ atoms and, if they have an average coordination number of 8, it may be reasonable to use $z = 4(P + Q)$. Remembering that the subscript c:a stands for the end-member $\mathrm{c}_{-\nu_{\mathrm{a}}}\mathrm{a}_{\nu_{\mathrm{c}}}$ and c:Va stands for $\mathrm{c}_1\mathrm{Va}_1$ we obtain the site fraction for a cation, A,

$$y_{\mathrm{A}} = \frac{\sum(-\nu_{\mathrm{a}})p_{\mathrm{A:a}} + Qp_{\mathrm{A:Va}}}{\sum\sum(-\nu_{\mathrm{a}})p_{\mathrm{c:a}} + Q\sum p_{\mathrm{c:Va}}} \qquad (60)$$

This is a more complicated expresion than Eq. (53) because the stoichiometric coefficients vary. In addition, Q contains y_{A} because it is defined as $\Sigma\nu_{\mathrm{c}}y_{\mathrm{c}}$. It will thus be complicated to give an explicit expression for y_{A} in terms of the p_{end} variables, which is necessary if they are chosen as the independent variables when minimizing the Gibbs energy. As an alternative one could choose the site fractions and the short range order parameter, ε, as the independent variables in the minimization procedure. Then one must express all the p_{end} quantities in terms of that set of variables which must be done by solving a system of equations like Eq. (60). As a simple example, it may be mentioned that the case $(\mathrm{A}^{\mathrm{a}}, \mathrm{B}^{\mathrm{b}})_P(\mathrm{D}^{-\mathrm{d}}, \mathrm{E}^{-\mathrm{e}})_Q$ yields

$$p_{\mathrm{A:D}} = y_{\mathrm{A}}y_{\mathrm{D}} + \varepsilon[y_{\mathrm{A}}y_{\mathrm{D}}(a-b)(d-e) - be] \qquad (61)$$

$$p_{\mathrm{A:E}} = y_{\mathrm{A}}y_{\mathrm{E}} + \varepsilon[y_{\mathrm{A}}y_{\mathrm{E}}(a-b)(d-e) + bd] \qquad (62)$$

$$p_{\mathrm{B:D}} = y_{\mathrm{B}}y_{\mathrm{D}} + \varepsilon[y_{\mathrm{B}}y_{\mathrm{D}}(a-b)(d-e) + ae] \qquad (63)$$

$$p_{\mathrm{B:E}} = y_{\mathrm{B}}y_{\mathrm{E}} + \varepsilon[y_{\mathrm{B}}y_{\mathrm{E}}(a-b)(d-e) - ad] \qquad (64)$$

to be compared with Eqs. (54)–(57). However, for a more general case this may become very complicated. It is thus highly desirable to find a method of introducing probabilities in such a way that Q does not appear in the primary expression for the cations. The site fractions could then be expressed directly in terms of the p_{end} variables using expressions corresponding to Eq. (60). The p_{end} quantities could then be used as the set of independent variables. The problem of Q in Eq. (60) arises from its introduction instead of ν_{c} in Eq. (46) when Eq. (47) was derived. An obvious possibility would thus be now to revert that modification when the p_{end} quantities are introduced. We would thus write the second summation in Eq. (59) as $\Sigma\nu_{\mathrm{c}}p_{\mathrm{c:Va}}\,\Delta_f{}^{\circ}G_{\mathrm{c}}$, obtaining

$$y_{\mathrm{A}} = \frac{\sum(-\nu_{\mathrm{a}})p_{\mathrm{A:a}} + \nu_{\mathrm{A}}p_{\mathrm{A:Va}}}{\sum\sum(-\nu_{\mathrm{a}})p_{\mathrm{c:a}} + \sum\nu_{\mathrm{c}}p_{\mathrm{c:Va}}} \qquad (65)$$

For species on the anion sublattice we would find

$$y_{\mathrm{D}} = \frac{\sum\nu_{\mathrm{c}}p_{\mathrm{c:D}}}{\sum\sum\nu_{\mathrm{c}}p_{\mathrm{c:a}} + \sum\nu_{\mathrm{c}}p_{\mathrm{c:Va}} + Q\sum p_{\mathrm{n}}} \qquad (66)$$

$$y_{\mathrm{Va}} = \frac{\sum\nu_{\mathrm{c}}p_{\mathrm{c:Va}}}{\sum\sum\nu_{\mathrm{c}}p_{\mathrm{c:a}} + \sum\nu_{\mathrm{c}}p_{\mathrm{c:Va}} + Q\sum p_{\mathrm{n}}} \qquad (67)$$

$$y_{\mathrm{N}} = \frac{Qp_{\mathrm{N}}}{\sum\sum\nu_{\mathrm{c}}p_{\mathrm{c:a}} + \sum\nu_{\mathrm{c}}p_{\mathrm{c:Va}} + Q\sum p_{\mathrm{n}}} \qquad (68)$$

but here the presence of Q does not cause much complications because Q only contains site fractions for the cations. It is also necessary to express the stoichiometric coefficients, P and Q, in terms of the p_{end} variables because they appear in the ideal entropy part of Eq. (59).

From their definitions, Eqs. (43) and (44), we find

$$Q = \sum \nu_c y_c = \frac{\sum\sum \nu_c(-\nu_a)p_{c:a} + (\nu_c)^2 p_{c:Va}}{\sum\sum(-\nu_a)p_{c:a} + \sum \nu_c p_{c:Va}} \tag{69}$$

$$\begin{aligned} P &= \sum(-\nu_a)y_a + Qy_{Va} \\ &= \frac{\sum\sum \nu_c(-\nu_a)p_{c:a} + Q\sum \nu_c p_{c:Va}}{\sum\sum \nu_c p_{c:a} + \sum \nu_c p_{c:Va} + Q\sum p_n} \end{aligned} \tag{70}$$

Selleby and Sundman (M. Selleby and B. Sundman, personal communication) found another alternative by comparing with an associate solution model where all the associates have one atom of the anion species. In order to make the expression hold for the same number of atoms as before, they multiplied by Q, obtaining instead of Eq. (59),

$$\begin{aligned} {}^{M}G_m = Q[&\sum\sum p_{c:a}\,\Delta_f{}^{\circ}G_{c_{-\nu_a/\nu_c}a_1} + \sum p_{c:Va}\,\Delta_f{}^{\circ}G_c \\ &+ \sum p_n\,\Delta_f{}^{\circ}G_n \\ &+ zRT[\sum\sum p_{c:a}\ln(Qp_{c:a}/\nu_c y_c y_a) \\ &+ \sum p_{c:Va}/y_c y_{Va})]] + RT[P\sum y_c \ln(y_c) \\ &+ Q\sum y_j \ln(y_j)] + {}^{E}G_m \end{aligned} \tag{71}$$

In order to make the comparison with Eq. (59) easier, we can rewrite the surface of reference as

$$\begin{aligned} G_m^{s.r.} = &\sum\sum(Q/\nu_c)p_{c:a}{}^{\circ}G_{c_{-\nu_a}a_{\nu_c}} + Q\sum p_{c:Va}{}^{\circ}G_c \\ &+ Q\sum p_n{}^{\circ}G_n \end{aligned} \tag{72}$$

The only modification of Eq. (59) is that $p_{c:a}$ has been replaced by $(Q/\nu_c)p_{c:a}$. This causes the $p_{c:a}$ quantities to be quite different and that will indirectly affect the values of $p_{c:Va}$ and p_n. The following expressions will now be obtained for the site fractions

$$y_A = \frac{(1/\nu_A)\sum(-\nu_a)p_{A:a} + p_{A:Va}}{\sum\sum(-\nu_a/\nu_c)p_{c:a} + \sum p_{c:Va}} \tag{73}$$

$$y_D = \sum p_{c:D} \tag{74}$$

$$y_{Va} = \sum p_{c:Va} \tag{75}$$

$$y_N = p_N \tag{76}$$

$$Q = \sum \nu_c y_c = \frac{\sum\sum(-\nu_a)p_{c:a} + \nu_c p_{c:Va}}{\sum\sum(-\nu_a/\nu_c)p_{c:a} + \sum p_{c:Va}} \tag{77}$$

$$\begin{aligned} P &= \sum(-\nu_a)y_a + Qy_{Va} \\ &= \sum\sum(-\nu_a)p_{c:a} + Q\sum p_{c:Va} \end{aligned} \tag{78}$$

The value of z in Eq. (71) should also be discussed. For Eq. (59) the value $4(P + Q)$ was proposed. In Eq. (71) z is already multiplied by Q and one could thus propose the value $4/(1 + P/Q)$. When including this model in the Thermo-Calc software package, Sundman entered z as a parameter that can be chosen freely. The model based on Eq. (59) after reverting the change from ν_c to Q has not yet been programmed.

It should again be mentioned that Dessureault and Pelton [35] took into account the effect of binary interaction parameters on the short range order in a reciprocal system. As described in Section 13 this can also be done with the compound energy formalism by substituting the appropriate p_{end} variable for products of y_i in the excess terms. There are a number of ways to do this, however. Finally, it should again be mentioned that Blander and Yosim [36] proposed that one could use the reciprocal parameter to approximate the effect of short range order in ionic melts.

15. Summary

The compound energy model has been developed step by step, taking into account various complicating aspects, and is now capable of describing the properties of many different types of phases. It is thus widely used in CALPHAD assessments although there are methods taking better account of short range order. However, they require more computing time and grow more complicated as the number of sublattices and components increases. It is hoped that the inclusion of a simple treatment of short range order in the compound energy formalism may be sufficient for most practical applications.

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References

[1] C. Wagner, W. Schottky, Z. Phys. Chem. B11 (1930) 163.
[2] A. Ölander, J. Am. Chem. Soc. 54 (1932) 3819.
[3] C.H. Johansson, Arch. Eisenhüttenw. 11 (1937/1938) 241.
[4] L. Kaufman, H. Bernstein, Computer Calculation of Phase Diagrams, Academic Press, New York, 1970.
[5] W.L. Bragg, E.J. Williams, Proc. R. Soc. A156 (1935) 540.
[6] M. Hillert, L.-I. Staffansson, Acta Chem. Scand. 24 (1970) 3618.
[7] H. Harvig, Acta Chem. Scand. 25 (1971) 3199.
[8] B. Sundman, J. Ågren, J. Phys. Chem. Solids 42 (1981) 297.
[9] J.-O. Andersson, A. Fernández-Guillermet, M. Hillert, B. Jansson, B. Sundman, Acta Metall. 34 (1986) 437.
[10] H.A. Bethe, Proc. R. Soc., (Lond.) A150 (1935) 552.
[11] O. Redlich, A. Kister, Ind. Eng. Chem. 40 (1948) 345.
[12] B. Sundman, B. Jansson, J.-O. Andersson, Calphad 9 (1985) 153.
[13] M. Hillert, Phase Equilibria, Phase Diagrams and Phase Transformations — Their Thermodynamic Basis, Cambridge University Press, Cambridge, 1998.

[14] M. Hillert, B. Burton, S.K. Saxena, S. Degterov, K.C.H. Kumar, H. Ohtani, F. Aldinger, A. Kussmaul, Calphad 21 (1997) 247.
[15] M. Hillert, Calphad 20 (1996) 333.
[16] B. Sundman, T. Mohri, Z. Metallkde. 81 (1990) 251.
[17] B. Sundman, S.G. Fries, W.A. Oates, Calphad 22 (1998) 335.
[18] I. Ansara, B. Sundman, P. Willemin, Acta Metall. 36 (1988) 977.
[19] I. Ansara, N. Dupin, H.L. Lukas, B. Sundman, J. Alloys Comp. 247 (1997) 20.
[20] Q. Chen, M. Hillert, J. Alloys Comp. 245 (1996) 125.
[21] T.I. Barry, A.T. Dinsdale, J.A. Gisby, B. Hallstedt, M. Hillert, B. Jansson, S. Jonsson, B. Sundman, J.R. Taylor, J. Phase Equil. 13 (1992) 459.
[22] M. Hillert, B. Jansson, J. Am. Ceram. Soc. 69 (1986) 732.
[23] Q. Chen, M. Hillert, B. Sundman, W.A. Oates, S.G. Fries, R. Schmid-Fetzer, J. Electr. Mater. 27 (1998) 961.
[24] M. Temkin, Acta Phys. Chim. USSR 20 (1945) 411.
[25] H. Flood, T. Förland, K. Grjotheim, Z. Anorg. Allg. Chem. 276 (1954) 289.
[26] M. Hillert, B. Jansson, B. Sundman, J. Ågren, Metall. Trans. 16A (1985) 137.
[27] B. Sundman, Calphad 15 (1991) 109.
[28] M. Selleby, M. Hillert, J. Phase Equil. 20 (1999) 288.
[29] M. Hillert, B. Jansson, B. Sundman, Metall. Trans. 218 (1990) 404.
[30] P. Dörner, L.J. Gauckler, H. Kried, H.L. Lukas, G. Petzow, J. Weiss, Calphad 3 (1979) 241.
[31] B. Hallstedt, M. Hillert, M. Selleby, B. Sundman, Calphad 18 (1994) 31.
[32] R. Kikuchi, Phys. Rev. 81 (1951) 998.
[33] A.E. Guggenheim, Mixtures, Clarendon Press, Oxford, 1952.
[34] B. Sundman, in: S. Nishiyama, H. Onodera (Eds.), Modelling and Simulation for Materials Design, CMSMD'96, NRIM, Japan, 1996, pp. 126–131.
[35] Y. Dessureault, A.D. Pelton, J. Chim. Phys. 88 (1991) 1811.
[36] M. Blander, S.J. Yosim, J. Chem. Phys. 39 (1963) 2610.