The Regular Solution Model for Stoichiometric Phases and Ionic Melts

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The regular solution model is developed for ionic melts and stoichiometric phases of the type $(A, B)_a (C, D)_c$ by a formal method. The validity of Flood's equation for exchange reactions in ionic melts is discussed in terms of this model. The model is also applied to phases which contain one substitutional and one interstitial solute. The vacancies in the interstitial sublattice is then regarded as an additional component of the system. Expressions for the integral and partial free energies are derived.

A stoichiometric phase can usually be regarded as composed of two sublattices, the sites of each one being occupied by a certain element. It is often possible to dissolve some amount of a new element by substituting one or the other of the main components. One may thus produce a ternary system composed of two sublattices one of them being filled by a mixture of two elements and the other one being filled by the third element. It has been suggested [1,2] that the thermodynamics of such a system can be described by the classical regular solution model if applied to the sublattice containing two elements. The same procedure should be applicable even if more than two elements are introduced into one sublattice. However, a new problem arises if both sublattices contain more than one element each. The simplest case can be represented by the formula $(A, B)_a (C,D)_c$.

A similar case is encountered in ionic melts containing at least two cations A and B and two anions C and D. A regular solution model for such ionic melts has been derived by Førland [3] as an extension of the quasithermodynamic theory of Flood, Førland and Grjotheim.[4] The theory of conformal ionic solutions by Blander [5] leads to the same model. The same expressions will now be derived by a simple, purely formal method, applicable to ionic melts as well as stoichiometric phases. It will also be shown how the model can be applied to interstitial solutions.

REPRESENTATION OF COMPOSITION

The coefficients in $(A, B)_a (C, D)_c$ express the number of sites in each sublattice and, for convenience, the size of the sublattices may be chosen such that $a + c = 1$. The number of moles of each kind of atom, n_A etc., are related by the following equation

$$n_e = n_A/a + n_B/a = n_C/c + n_D/c \tag{1}$$

where n_e represents the size of the system.

In ionic melts containing at least two cations, A and B, and two anions, C and D, the requirement of electroneutrality yields the relation

$$n_e = n_A/a + n_B/b = n_C/c + n_D/d \tag{2}$$

where, for convenience, the quantities $1/a$ etc. can be identified with the valence of each ion. The size of the system, n_e is then expressed as the number of equivalents.

It is usual to express the concentration of a certain element by its mole fraction,

$$X_A = \frac{n_A}{n_A + n_B + n_C + n_D}; \quad \sum X_A = 1 \tag{3}$$

For an ionic melt, it is sometimes convenient to define the mole fractions separately for the cations and for the anions.

$$Y_A = \frac{n_A}{n_A + n_B}; \quad Y_A + Y_B = 1 \tag{4}$$

$$Y_C = \frac{n_C}{n_C + n_D}; \quad Y_C + Y_D = 1 \tag{5}$$

It is also convenient to define corresponding fractions taking into account the charge of the ions,

$$Z_A = \frac{n_A/a}{n_A/a + n_B/b} = \frac{n_A}{a \, n_e}; \quad Z_A + Z_B = 1 \tag{6}$$

$$Z_C = \frac{n_C/c}{n_C/c + n_D/d} = \frac{n_C}{c \, n_e}; \quad Z_C + Z_D = 1 \tag{7}$$

The corresponding quantities for a stoichiometric phase are related in the following way in view of $b = a$ and $d = c$.

$$Z_A = Y_A = X_A \frac{a+c}{a}; \quad Z_B = Y_B = X_B \frac{a+c}{a} \tag{8}$$

$$Z_C = Y_C = X_C \frac{a+c}{c}; \quad Z_D = Y_D = X_D \frac{a+c}{c} \tag{9}$$

In the systems under consideration there are four elements but in view of relation (1) or (2) the degrees of freedom in varying the composition is one less than in an ordinary quaternary system. The variation in composition can thus be represented by two parameters and the composition is conveniently plotted on a square where the corners represent the four basic compounds A_aC_c, A_aD_d, B_bC_c, and B_bD_d and the parameters Z_B and Z_D are used to represent the composition of any intermediate point;[6] Fig. 1.
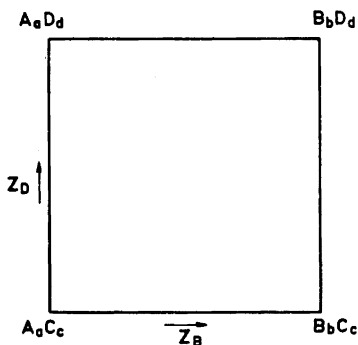

Fig. 1. Representation of composition in a quaternary system where the components mix with each other, two and two.

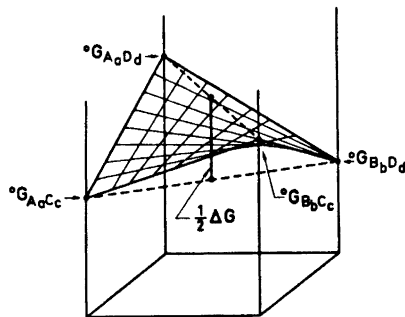*Fig. 2.* Suggested surface of reference for the free energy in a quaternary system where the components mix with each other two and two.

Temkin [7] proposed that the entropy of mixing of an ionic melt can be calculated under the assumption that the anions mix randomly with each other and the cations with each other. This model gives the following expression,

$$-S^{ideal}/R = n_A \ln Y_A + n_B \ln Y_B + n_c \ln Y_C + n_D \ln Y_D \qquad (10)$$

or, by dividing with the size of the system as defined by n_c from eqn. (2)

$$-S_m^{ideal}/R = aZ_A \ln Y_A + bZ_B \ln Y_B + cZ_C \ln Y_C + dZ_D \ln Y_D \qquad (11)$$

The same equations with $a = b$ and $c = d$ hold for a stoichiometric phase if the atoms mix randomly within each sublattice.

STATES OF REFERENCE FOR THE FREE ENERGY

In multicomponent systems it is usual to define an excess free energy, $^E G_m$, by the following expression

$$G_m = \sum_i X_i {}^\circ G_i - T S_m^{ideal} + {}^E G_m \qquad (12)$$

where the quantities $^\circ G_i$ are the free energies of the pure components. They thus define the natural plane of reference for the free energy. As an exemple, a ternary system has three states of reference and they define a plane of

reference. In the systems now under consideration there are four states of reference, one each for the compounds A_aC_c, A_aD_d, B_bC_c, and B_bD_d, and it will generally be impossible to construct a plane of reference through all of them. It thus seems to be necessary to choose a non-planar surface of reference. The simplest geometric shape is the one defined by the following choice.

$$G_m = Z_A Z_C {}^\circ G_{A_aC_c} + Z_A Z_D {}^\circ G_{A_aD_d} + Z_B Z_C {}^\circ G_{B_bC_c} + Z_B Z_D {}^\circ G_{B_bD_d} - TS_m^{\text{ideal}} + {}^E G_m \quad (13)$$

where $Z_A Z_C {}^\circ G_{A_aC_c} + Z_A Z_D {}^\circ G_{A_aD_d} + Z_B Z_C {}^\circ G_{B_bC_c} + Z_B Z_D {}^\circ G_{B_bD_d}$ represents the surface of reference. It is illustrated by Fig. 2 and its deviation from a plane shape is defined by the following quantity,

$$\Delta G = {}^\circ G_{A_aD_d} + {}^\circ G_{B_bC_c} - {}^\circ G_{A_aC_c} - {}^\circ G_{B_bD_d} \quad (14)$$

POWER SERIES REPRESENTATION OF EXCESS FREE ENERGY

In an ordinary multicomponent system the excess free energy is often represented by a power series. As can be seen from eqn. (12), however, first power terms are already used in defining the plane of reference. The expression for the excess free energy therefore starts with second power terms which define the regular solution model

$$^E G_m = \sum X_i X_j \; K_{ij} \quad (15)$$

For the systems now under consideration eqn. (13) shows that four of the second power terms are already used in defining the surface of reference. The excess free energy for a simple case could possibly be described by the remaining two terms of the same power,

$$^E G_m = Z_A Z_B \; K_{AB} + Z_C Z_D \; K_{CD} \quad (16)$$

However, it seems rather improbable that the interaction between the A and B atoms should be quite independent of whether the other sublattice is occupied by C or D atoms. It may thus be suggested that a regular solution model for these systems should be defined by the following expression

$$^E G_m = Z_A Z_B Z_C \; L_{AB}{}^C + Z_A Z_B Z_D \; L_{AB}{}^D + Z_C Z_D Z_A \; L_{CD}{}^A + Z_C Z_D Z_B \; L_{CD}{}^B \quad (17)$$

EXPRESSIONS FOR THE PARTIAL FREE ENERGIES

The partial quantities can be derived from the integral quantities of eqns. (11) and (13) by standard methods, yielding the following rule of calculation with our choice of composition variables

$$\overline{G}_{A_aC_c} = G_m + (1 - Z_A) \frac{\partial G_m}{\partial Z_A} + (1 - Z_C) \frac{\partial G_m}{\partial Z_C} \quad (18)$$

The following expressions are obtained using ΔG from eqn. (14).

$$\overline{G}_{A_aC_c} = {}^\circ G_{A_aC_c} + Z_B Z_D \; \Delta G + RT a \ln Y_A + RT c \ln Y_C + {}^E G_{A_aC_c} \quad (19)$$

$$\overline{G}_{A_aD_d} = {}^\circ G_{A_aD_d} - Z_B Z_C \; \Delta G + RT a \ln Y_A + RT d \ln Y_D + {}^E G_{A_aD_d} \quad (20)$$

$$\overline{G}_{B_bC_c} = {}^\circ G_{B_bC_c} - Z_A Z_D \, \Delta G + RTb \ln Y_B + RTc \ln Y_C + {}^E G_{B_bC_c} \tag{21}$$

$$\overline{G}_{B_bD_d} = {}^\circ G_{B_bD_d} + Z_A Z_C \, \Delta G + RTb \ln Y_B + RTd \ln Y_D + {}^E G_{B_bD_d} \tag{22}$$

The well-known fact that these partial quantities can be obtained from a free energy diagram by constructing a plane of tangency and reading its intersections with the component axes, immediately shows that the following relations hold.

$$\overline{G}_{A_aD_d} + \overline{G}_{B_bC_c} - \overline{G}_{A_aC_c} - \overline{G}_{B_bD_d} = 0 \tag{23}$$

$$ {}^E G_{A_aD_d} + {}^E G_{B_bC_c} - {}^E G_{A_aC_c} - {}^E G_{B_bD_d} = 0 \tag{24}$$

It is also of considerable interest to study the change in free energy if component B is exchanged with the corresponding amount of component A, *i.e.* $dn_A/a = -dn_B/b$ and $dn_e = 0$ in view of eqn. (2). This change may be accomplished in two ways, either by adding A_aC_c and removing B_bC_c or by adding A_aD_d and removing B_bD_d. With the first alternative one obtains

$$\left(\frac{\partial G}{\partial n_A/a}\right)_{n_e, n_C} = \overline{G}_{A_aC_c} - \overline{G}_{B_bC_c} = Z_C({}^\circ G_{A_aC_c} - {}^\circ G_{B_bC_c}) + Z_D({}^\circ G_{A_aD_d} - {}^\circ G_{B_bD_d}) +$$

$$+ RTa \ln Y_A - RTb \ln Y_B + {}^E G_{A_aC_c} - {}^E G_{B_bC_c} \tag{25}$$

It may be pointed out that this partial derivative of the total free energy is identical to $(\partial G_m/\partial Z_A)_{Z_C}$ which in some cases may provide a simpler way of calculation.

An analogous expression is obtained for the exchange of component D with component C,

$$\left(\frac{\partial G}{\partial n_C/c}\right)_{n_e, n_A} = \overline{G}_{A_aC_c} - \overline{G}_{A_aD_d} = Z_A({}^\circ G_{A_aC_c} - {}^\circ G_{A_aD_d}) + Z_B({}^\circ G_{B_bC_c} - {}^\circ G_{B_bD_d})$$

$$+ RTc \ln Y_C - RTd \ln Y_D + {}^E G_{A_aC_c} - {}^E G_{A_aD_d} \tag{26}$$

The expression for the excess free energy defined by eqn. (16) gives the following partial quantities,

$$ {}^E G_{A_aC_c} = Z_B{}^2 K_{AB} + Z_D{}^2 K_{CD} \tag{27}$$

$$ {}^E G_{A_aD_d} = Z_B{}^2 K_{AB} + Z_C{}^2 K_{CD} \tag{28}$$

$$ {}^E G_{B_bC_c} = Z_A{}^2 K_{AB} + Z_D{}^2 K_{CD} \tag{29}$$

$$ {}^E G_{B_bD_d} = Z_A{}^2 K_{AB} + Z_C{}^2 K_{CD} \tag{30}$$

$$ {}^E G_{A_aC_c} - {}^E G_{A_aD_d} = {}^E G_{B_bC_c} - {}^E G_{B_bD_d} = (Z_D - Z_C) \, K_{CD} \tag{31}$$

$$ {}^E G_{A_aC_c} - {}^E G_{B_bC_c} = {}^E G_{A_aD_d} - {}^E G_{B_bD_d} = (Z_B - Z_A) \, K_{AB} \tag{32}$$

The more complicated expression for the excess free energy defined by eqn. (17) gives the following partial quantities.

$$ {}^E G_{A_aC_c} = Z_B(Z_D Z_A + Z_B Z_C)L_{AB}{}^C + Z_D(Z_D Z_A + Z_B Z_C)L_{CD}{}^A + Z_B Z_D(Z_D - Z_C)L_{CD}{}^B$$

$$+ Z_B Z_D(Z_B - Z_A)L_{AB}{}^D \tag{33}$$

$$^E G_{A_aD_d} = Z_B Z_C (Z_B - Z_A) L_{AB}{}^C + Z_C(Z_C Z_A + Z_B Z_D) L_{CD}{}^A + Z_B Z_C(Z_C - Z_D) L_{CD}{}^B +$$
$$+ Z_B(Z_C Z_A + Z_B Z_D) L_{AB}{}^D \tag{34}$$

$$^E G_{B_bC_c} = Z_A(Z_D Z_B + Z_A Z_C) L_{AB}{}^C + Z_A Z_D(Z_D - Z_C) L_{CD}{}^A + Z_D(Z_D Z_B + Z_A Z_C) L_{CD}{}^B$$
$$+ Z_A Z_D(Z_A - Z_B) L_{AB}{}^D \tag{35}$$

$$^E G_{B_bD_d} = Z_A Z_C(Z_A - Z_B) L_{AB}{}^C + Z_A Z_C(Z_C - Z_D) L_{CD}{}^A + Z_C(Z_C Z_B + Z_A Z_D) L_{CD}{}^B$$
$$+ Z_A(Z_C Z_B + Z_A Z_D) L_{AB}{}^D \tag{36}$$

$$^E G_{A_aC_c} - {}^E G_{A_aD_d} = Z_B Z_A L_{AB}{}^C + Z_B(Z_D - Z_C) L_{CD}{}^B + Z_A(Z_D - Z_C) L_{CD}{}^A - Z_A Z_B L_{AB}{}^D \tag{37}$$

$$^E G_{A_aC_c} - {}^E G_{B_bC_c} = Z_C(Z_B - Z_A) L_{AB}{}^C - Z_C Z_D L_{CD}{}^B + Z_D Z_C L_{CD}{}^A + Z_D(Z_B - Z_A) L_{AB}{}^D \tag{38}$$

APPLICATION TO IONIC SALT MELTS

Flood et al.[4] suggested that the change in free energy when the ion B is exchanged with ion A can be evaluated by the following expression

$$(\partial G_m / \partial Z_A)_{Z_1, Z_2} = \sum_i Z_i \, (\partial G_m / \partial Z_A)_{Z_1, Z_2, \ldots}{}^{Z_i = 1} \tag{39}$$

The summation is carried out over all the ions of the opposite charge, here denoted by 1, 2, 3, etc., and there is no limitation to the number of such ions. The superscript $Z_i = 1$ indicates that the derivative should be evaluated at this value.

For the case of two anions and two cations eqn. (25) yields the following expressions,

$$\left(\frac{\partial G_m}{\partial Z_A} \right)_{Z_C}^{Z_C = 1} = {}^\circ G_{A_aC_c} - {}^\circ G_{B_bC_c} + RT \text{a} \ln Y_A - RT\text{b} \ln Y_B + {}^E G_{A_aC_c}{}^{Z_C = 1} - {}^E G_{B_bC_c}{}^{Z_C = 1} \tag{40}$$

$$\left(\frac{\partial G_m}{\partial Z_A} \right)_{Z_C}^{Z_D = 1} = {}^\circ G_{A_aD_d} - {}^\circ G_{B_bD_d} + RT \text{a} \ln Y_A - RT\text{b} \ln Y_B + {}^E G_{A_aC_c}{}^{Z_D = 1} - {}^E G_{B_bC_c}{}^{Z_D = 1} \tag{41}$$

and by combination with eqn. (25) one obtains,

$$\left(\frac{\partial G_m}{\partial Z_A} \right)_{Z_C} = Z_C \left(\frac{\partial G_m}{\partial Z_A} \right)_{Z_C}^{Z_C = 1} + Z_D \left(\frac{\partial G_m}{\partial Z_A} \right)_{Z_C}^{Z_D = 1} - Z_C {}^E G_{A_aC_c}{}^{Z_C = 1} + Z_C {}^E G_{B_bC_c}{}^{Z_C = 1}$$
$$- Z_D {}^E G_{A_aC_c}{}^{Z_D = 1} + Z_D {}^E G_{B_bC_c}{}^{Z_D = 1} + {}^E G_{A_aC_c} - {}^E G_{B_bC_c} \tag{42}$$

Flood's expression thus neglects a series of excess free energy terms. However, the sum of these terms will only be $Z_C Z_D (L_{CD}{}^A - L_{CD}{}^B)$ according to the regular solution model defined by eqn. (17) and it will be zero according to the model defined by eqn. (16). It thus seems that Flood's expression might be very realistic for many cases.

APPLICATION TO AN INTERSTITIAL AND SUBSTITUTIONAL SOLUTION

An interstitial solution can be regarded as composed of two sublattices. One of them is completely filled by the base element and any substitutionally dissolved element. The other sublattice is only partially filled by the interstitially dissolved element. However, it is possible to regard the vacancies in the interstitial sublattice as a component and the whole system, containing a base element A, a substitutional addition B and an interstitial addition C, can thus be represented as a stoichiometric phase, $(A,B)_a (C, V)_c$ where V stands for the vacancies and $a + c = 1$.

The equations, derived for a stoichiometric phase, can thus be applied to this kind of system as well. The mole fractions should then be redefined, taking into account the presence of the vacancies.[8]

$$X_1 = aX_A/(1 - X_C) \tag{43}$$

$$X_2 = aX_B/(1 - X_C) \tag{44}$$

$$X_3 = aX_C/(1 - X_C) \tag{45}$$

$$X_4 = c - aX_C/(1 - X_C) \tag{46}$$

The relation of these variables to those defined for a stoichiometric phase is obtained by inserting X_1 instead of X_A in eqns. (8) and (9), yielding

$$Z_A = Y_A = X_1/a = X_A/(1 - X_C) \tag{47}$$

$$Z_B = Y_B = X_2/a = X_B/(1 - X_C) \tag{48}$$

$$Z_C = Y_C = X_3/c = (a/c)X_C/(1 - X_C) \tag{49}$$

$$Z_V = Y_V = X_4/c = 1 - (a/c)X_C/(1 - X_C) \tag{50}$$

It may thus be advantageous to present the composition of a ternary system $A - B - C$ on a square like Fig. 1 and using $X_B/(1 - X_C)$ and $(a/c)X_C/(1 - X_C)$ as the variables.

It should further be noticed that the expressions derived for the molar quantities must be multiplied by $(1 - X_C)/a$ in order to hold for one mole of real material.

It may for instance be instructive to discuss how the four terms in eqn. (13), defining the surface of reference, are transformed. We find

$$\sum Z_i Z_j {}^\circ G_{ij}(1 - X_C)/a = X_A {}^\circ G_{A_aV_c}/a + X_B {}^\circ G_{B_aV_c}/a + X_C({}^\circ G_{A_aC_c} - {}^\circ G_{A_aV_c})/c +$$

$$+ \frac{X_B X_C}{1 - X_C} \, \Delta G/c \tag{51}$$

The quantity ${}^\circ G_{A_aV_c}/a$ is identical to ${}^\circ G_A$, the free energy of one mole of pure A, because the "compound" A_aV_c is nothing but pure A. By the same reason ${}^\circ G_{B_aV_c}/a$ is identical to ${}^\circ G_B$. However, it is not possible to identify any term in (51) as representing the free energy of one mole of pure C because pure C cannot exist according to our model, C being an interstitially dissolved element. Instead, our model leads to an artificial standard state of C for the

solution of C in A and the expression $(^\circ G_{\text{A}_a\text{C}_c} - {}^\circ G_{\text{A}_a\text{V}_c})/c$ represents its molar free energy.

In the same way, the molar free energy of the corresponding standard state for the solution of C in B is equal to $(^\circ G_{\text{B}_a\text{C}_c} - {}^\circ G_{\text{B}_a\text{V}_c})/c$. The definition of ΔG in eqn. (14) shows that the factor $\Delta G/c$ in the last term of (51) represents the difference between the two artificial standard states for C now mentioned.

The two excess free energy terms of eqn. (16) will transform to the following shape

$$(Z_\text{A} Z_\text{B} K_\text{AB} + Z_\text{C} Z_\text{D} K_\text{CD})(1 - X_\text{C})/a = \frac{X_\text{A} X_\text{B}}{1 - X_\text{C}} K_\text{AB}/a + X_\text{C}\left(1 - \frac{a}{c}\frac{X_\text{C}}{1 - X_\text{C}}\right)K_\text{CV}/c \tag{52}$$

As expected the first term describes the interaction between the two elements in the main lattice and the second term describes the interaction within the interstitial sublattice. These interactions may depend upon the elements present in the other sublattice as described in the model defined by eqn. (17), yielding the following more complicated expression.

$$\frac{a}{c}\frac{X_\text{C}}{1 - X_\text{C}}\frac{X_\text{A} X_\text{B}}{1 - X_\text{C}} L_\text{AB}{}^\text{C}/a + \left(1 - \frac{a}{c}\frac{X_\text{C}}{1 - X_\text{C}}\right)\frac{X_\text{A} X_\text{B}}{1 - X_\text{C}} L_\text{AB}{}^\text{V}/a +$$
$$+ X_\text{A} \frac{X_\text{C}}{1 - X_\text{C}}\left(1 - \frac{a}{c}\frac{X_\text{C}}{1 - X_\text{C}}\right)L_\text{CV}{}^\text{A}/c + X_\text{B} \frac{X_\text{C}}{1 - X_\text{C}}\left(1 - \frac{a}{c}\frac{X_\text{C}}{1 - X_\text{C}}\right)L_\text{CV}{}^\text{B}/c \tag{53}$$

G_m for a system $\text{A} - \text{B} - \text{C}$ according to this regular solution model is described by the sum of (51) and (53) and the ideal entropy.

The partial quantities can be obtained from eqns. (20), (22), and (26) by inserting the expressions for the excess free energy, eqns. (34), (36), and (37).

$$\overline{G}_\text{A} = \frac{1}{a}\overline{G}_{\text{A}_a\text{V}_c} = {}^\circ G_\text{A} + RT \ln Y_\text{A} + RT\frac{c}{a}\ln (1 - Y_\text{C}) + {}^\text{E}G_\text{A} \tag{54}$$

$$\overline{G}_\text{B} = \frac{1}{a}\overline{G}_{\text{B}_a\text{V}_c} = {}^\circ G_\text{B} + RT \ln Y_\text{B} + RT\frac{c}{a}\ln (1 - Y_\text{C}) + {}^\text{E}G_\text{B} \tag{55}$$

$$\overline{G}_\text{C} = \frac{1}{c}\left(\frac{\partial G}{\partial n_\text{c}/c}\right)_{n_\text{c, A}} = {}^\circ G_\text{C} + RT \ln Y_\text{C}/(1 - Y_\text{C}) + {}^\text{E}G_\text{C} \tag{56}$$

where

$$a^\text{E}G_\text{A} = - Y_\text{B} Y_\text{C}(\Delta G + L_\text{AB}{}^\text{C} - L_\text{AB}{}^\text{V} + L_\text{CV}{}^\text{B} - L_\text{CV}{}^\text{A}) + Y_\text{B}{}^2 L_\text{AB}{}^\text{V} + Y_\text{C}{}^2 L_\text{CV}{}^\text{A} +$$
$$+ Y_\text{B}{}^2 Y_\text{C} 2(L_\text{AB}{}^\text{C} - L_\text{AB}{}^\text{V}) + Y_\text{B} Y_\text{C}{}^2 2(L_\text{CV}{}^\text{B} - L_\text{CV}{}^\text{A}) \tag{57}$$

$$a^\text{E}G_\text{B} = Y_\text{A} Y_\text{C}(\Delta G + L_\text{AB}{}^\text{V} - L_\text{AB}{}^\text{C} + L_\text{CV}{}^\text{B} - L_\text{CV}{}^\text{A}) + Y_\text{A}{}^2 L_\text{AB}{}^\text{V} + Y_\text{C}{}^2 L_\text{CV}{}^\text{B} +$$
$$+ Y_\text{A}{}^2 Y_\text{C} 2(L_\text{AB}{}^\text{C} - L_\text{AB}{}^\text{V}) + Y_\text{A} Y_\text{C}{}^2 2(L_\text{CV}{}^\text{A} - L_\text{CV}{}^\text{B}) \tag{58}$$

$$c^\text{E}G_\text{C} = Y_\text{B}(\Delta G + L_\text{AB}{}^\text{C} - L_\text{AB}{}^\text{V} + L_\text{CV}{}^\text{B} - L_\text{CV}{}^\text{A}) - Y_\text{C} 2 L_\text{CV}{}^\text{A} +$$
$$+ Y_\text{B} Y_\text{C} 2(L_\text{CV}{}^\text{A} - L_\text{CV}{}^\text{B}) + Y_\text{B}{}^2(L_\text{AB}{}^\text{V} - L_\text{AB}{}^\text{C}) \tag{59}$$

$$c^\circ G_\text{C} = {}^\circ G_{\text{A}_a\text{C}_c} - {}^\circ G_{\text{A}_a\text{V}_c} + L_\text{CV}{}^\text{A} \tag{60}$$

It is interesting to note that all the parameters used can in principle be determined from experimental information on the binary system AB and information on $\overline{G}_C$ for the ternary system.

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