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PARTIAL GIBBS ENERGIES FROM REDLICH–KISTER POLYNOMIALS

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ABSTRACT

According to Redlich and Kister the polynomial representation of the excess Gibbs energy of a binary system should be written in a special form in order to be useful for predicting the properties in a higher-order system. General expressions for partial Gibbs energies are now derived from the Redlich–Kister polynomial for substitutional and interstitial solutions, and for the more general case of solution phases with two sublattices.

INTRODUCTION

It is a common procedure to represent the excess molar Gibbs energy of a binary solution with a so-called Redlich–Kister polynomial

$$^{E}G_{m} = x_1 x_2 \sum_{0}^{n} {}^{k}L_{12}(x_1 - x_2)^k \tag{1}$$

This expression seems to have been first used by Guggenheim [1] but Redlich and Kister [2] were the first ones to suggest that this form should be used to represent the binary contributions to the thermodynamic properties of higher-order systems. For such an application all the various polynomials used for binary systems yield different results because $x_1 + x_2$ is no longer equal to 1 [3].

Expressions for the Gibbs energy of higher order systems, based upon binary properties, are today in frequent use for predicting thermodynamic properties as well as phase equilibria and complete phase diagrams. Most of that work is carried out with computers and there are many programs available which operate directly on the molar Gibbs energy. It should thus be unnecessary to elaborate eqn. (1) further; on the other hand, the literature is still full of lengthy derivations of expressions for partial Gibbs energies based upon various slight modifications of eqn. (1). It would thus

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seem justified to present a derivation for the general case, once and for all. Such a derivation will now be presented. It will first be carried out without using the simplifications possible in a binary system where $x_1 + x_2 = 1$. The result will thus be applicable to higher-order systems as well. Furthermore, solution phases with two sublattices will be treated, with special emphasis on interstitial solutions.

SUBSTITUTIONAL SOLUTION

The partial Gibbs energy of an element i will be derived using the well-known relation

$$G_i = G_m + \partial G_m/\partial x_i - \sum x_l \partial G_m/\partial x_l \tag{2}$$

Applying this relation to the excess Gibbs energy given by eqn. (1) we can evaluate the contribution from interactions between two elements in a substitutional solution

$$\begin{aligned} {}^{E}G_i^1 &= {}^{0}L_{ij}(x_i x_j + x_j - 2x_i x_j) + \sum_1^n {}^{k}L_{ij}\big[x_i x_j (x_i - x_j)^k + x_j (x_i - x_j)^k \\ &\quad + k x_i x_j (x_i - x_j)^{k-1} - 2x_i x_j (x_i - x_j)^k \\ &\quad - k x_i x_j (x_i - x_j)^{k-1}(x_i - x_j)\big] \\ &= {}^{0}L_{ij} x_j (1 - x_i) + \sum_1^n {}^{k}L_{ij} x_j (x_i - x_j)^{k-1}\big[(1 - x_i)(1 + k)(x_i - x_j) + k x_j\big] \end{aligned} \tag{3}$$

For the contribution to the partial Gibbs energy of i from the interaction between two other elements, l and j, we obtain

$$\begin{aligned} {}^{E}G_i^2 &= {}^{0}L_{lj}(x_l x_j - 2x_l x_j) + \sum_1^n {}^{k}L_{lj}\big[x_l x_j (x_l - x_j)^k - 2x_l x_j (x_l - x_j)^k \\ &\quad - k x_l x_j (x_l - x_j)^{k-1}(x_l - x_j)\big] \\ &= -x_l x_j \left[{}^{0}L_{lj} + \sum_1^n {}^{k}L_{lj}(x_l - x_j)^k (1 + k)\right] \end{aligned} \tag{4}$$

For a multicomponent system we should add contributions from all binary interactions as given by eqns. (3) and (4). For a binary A–B system we can replace $1 - x_A$ by x_B and $1 - x_B$ by x_A and obtain from eqn. (3)

$${}^{E}G_A = x_B^2\left\{{}^{0}L_{AB} + \sum_1^n {}^{k}L_{AB}(x_A - x_B)^{k-1}\big[(2k+1)x_A - x_B\big]\right\} \tag{5}$$

$${}^{E}G_B = x_A^2\left\{{}^{0}L_{AB} + \sum_1^n {}^{k}L_{AB}(x_A - x_B)^{k-1}\big[x_A - (2k+1)x_B\big]\right\} \tag{6}$$

It should be noted that according to our notation ${}^kL_{BA} = -{}^kL_{AB}$ for odd k values.

PHASES WITH TWO SUBLATTICES

In the same way one could derive expressions for a phase with two sublattices. One would then have to consider the interaction between two elements on one sublattice but also take into account the possibility that the strength of this interaction depends upon what element occupies the other sublattice. Such an interaction parameter may be denoted by L_{ij}^{M} and its contribution to the excess Gibbs energy of one mole of formula units would be [4]

$$ {}^{E}G_{m}^{1} = y_M y_i y_j \sum_{0}^{n} {}^kL_{ij}^{M} (y_i - y_j)^k \tag{7} $$

y is here the site fraction, i.e. mole fraction defined for each sublattice separately. The partial Gibbs energy for a compound $M_a i_c$ is obtained from

$$ {}^{E}G_{Mi} = {}^{E}G_m - \sum y \partial {}^{E}G_m / \partial y + \partial {}^{E}G_m / \partial y_M + \partial {}^{E}G_m / \partial y_i \tag{8} $$

There will be contributions from four types of terms, originating from the interactions L_{ij}^{M}, L_{ij}^{N}, L_{lj}^{M} and L_{lj}^{N}. They give the following expressions

$$ {}^{E}G_{Mi}^{1} = {}^0L_{ij}^{M} y_j (y_i + y_M - 2 y_i y_M) + \sum_{1}^{n} {}^kL_{ij}^{M} (y_i - y_j)^{k-1} y_j $$
$$ \times \{ (y_i - y_j)[y_M (1+k)(1-y_i) + y_i - y_M y_i] + k y_M y_j \} \tag{9} $$

$$ {}^{E}G_{Mi}^{2} = {}^0L_{ij}^{N} y_N y_j (1 - 2y_i) + \sum_{1}^{n} {}^kL_{ij}^{N} (y_i - y_j)^{k-1} y_N y_j $$
$$ \times \{ (y_i - y_j)[(1+k)(1-y_i) - y_i] + k y_j \} \tag{10} $$

$$ {}^{E}G_{Mi}^{3} = {}^0L_{lj}^{M} y_l y_j (1 - 2y_M) + \sum_{1}^{n} {}^kL_{lj}^{M} (y_l - y_j)^k y_l y_j (1 - 2y_M - k y_M) \tag{11} $$

$$ {}^{E}G_{Mi}^{4} = {}^0L_{lj}^{N} y_N y_l y_j (-2) + \sum_{1}^{n} {}^kL_{lj}^{N} (y_l - y_j)^k y_N y_l y_j (-2 - k) \tag{12} $$

Equivalent terms would come from the interactions on the first sublattice, L_{MN}^{i}, L_{MN}^{j}, L_{KN}^{i} and L_{KN}^{j}. Of course, the total value of ${}^{E}G_{Mi}$ is obtained by adding these expressions for all the interactions in the system. For a ternary M–C–D system with two elements C and D on one sublattice, one has $y_C + y_D = 1$ and obtains

$$ {}^{E}G_{MC} = y_D^2 \left\{ {}^0L_{CD}^{M} + \sum_{1}^{n} {}^kL_{CD}^{M} (y_C - y_D)^{k-1} [(2k+1) y_C - y_D] \right\} \tag{13} $$

$$ {}^{E}G_{MD} = y_C^2 \left\{ {}^0L_{CD}^{M} + \sum_{1}^{n} {}^kL_{CD}^{M} (y_C - y_D)^{k-1} [y_C - (2k+1) y_D] \right\} \tag{14} $$

INTERSTITIAL SOLUTIONS

For an interstitial solution there are some vacant sites on one sublattice as illustrated by the formula $M_a(I,Va)_c$. Equations (9)–(12) still apply if we treat the vacancy as an element. In this case ${}^EG_{MVa}$ is identical to $a{}^EG_M$ since there are a moles of M in each mole of formula units. In order to evaluate the excess partial Gibbs energy for an interstitial element i one must take the difference between ${}^EG_{Mi}$ and ${}^EG_{MVa}$. In this case there would be eight types of terms originating from L^M_{ij}, L^N_{ij}, L^M_{lj}, L^N_{lj}, L^M_{iVa}, L^N_{iVa}, L^M_{lVa} and L^N_{lVa}. However, for L^M_{lj} and L^N_{lj} the contributions to ${}^EG_{Mi}$ and ${}^EG_{MVa}$ will be identical and will disappear when the difference is taken, a fact which is evident from the following procedure of calculation which results directly from eqn. (8)

$$c{}^EG_i = {}^EG_{Mi} - {}^EG_{MVa} = \partial{}^EG_m/\partial y_i - \partial{}^EG_m/\partial y_{Va} \tag{15}$$

It is immediately evident that there will be no contribution from L^M_{lj} and L^N_{lj}. The following contributions are obtained

$$c{}^EG_i^1 = {}^0L^M_{iVa}y_M(y_{Va} - y_i) + \sum_1^n {}^kL^M_{iVa}y_M(y_i - y_{Va})^{k-1} \times\left[2ky_iy_{Va} - (y_i - y_{Va})^2\right] \tag{16}$$

$$c{}^EG_i^2 = {}^0L^M_{ij}y_My_j + \sum_1^n {}^kL^M_{ij}y_My_j(y_i - y_j)^{k-1}\left[(k+1)y_i - y_j\right] \tag{17}$$

$$c{}^EG_i^3 = {}^0L^M_{lVa}y_My_l(-1) + \sum_1^n {}^kL^M_{lVa}y_My_l(y_l - y_{Va})^{k-1}\left[y_l - (k+1)y_{Va}\right] \tag{18}$$

The three contributions from L^N_{iVa}, L^N_{ij} and L^N_{lVa} are obtained by simply inserting y_N instead of y_M in eqns. (16)–(18). In addition there may be interactions on the first sublattice that yield contributions of the form

$$c{}^EG_i^4 = \left(L^i_{KN} - L^{Va}_{KN}\right)y_Ky_N(y_K - y_N)^k \tag{19}$$

For a binary interstitial solution represented with the formula $M_a(C,Va)_c$ we obtain after using $y_C - y_{Va} = 1$

$$a{}^EG_M = y_C^2\left\{{}^0L^M_{VaC} + \sum_1^n {}^kL^M_{VaC}(1 - 2y_C)^{k-1}[2k + 1 - 2y_C(k+1)]\right\} \tag{20}$$

$$c{}^EG_C = {}^0L^M_{VaC}(1 - 2y_C) + \sum_1^n {}^kL^M_{VaC}(1 - 2y_C)^{k-1} \times\left[1 - 2y_C(k+2) + 2y_C^2(k+2)\right] \tag{21}$$

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