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Extension of Darken's Quadratic Formalism to Dilute Multicomponent Solutions

S. SRIKANTH and K. T. JACOB

Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India.

Darken's quadratic formalism is extended to multicomponent solutions. Equations are developed for the representation of the integral and partial excess free energies, entropies and enthalpies in dilute multicomponent solutions. Quadratic formalism applied to multicomponent solutions is thermodynamically consistent. The formalism is compared with the conventional second order Maclaurin series or interaction parameter representation and the relations between them are derived. Advantages of the quadratic formalism are discussed.

KEY WORDS: quadratic formalism; interaction parameters; enthalpy and entropy parameters; thermodynamic consistency.

1. Introduction

Darken[1,2] in a sequence of two papers developed a quadratic formalism for the representation of the excess integral and partial free energies in binary and ternary systems in the vicinity of a single component selected as the solvent. In the first paper,[1] Darken suggested that for most liquid binary metallic systems, the thermodynamic behaviour in the two terminal regions is relatively simple and the activity coefficients of the solvent and solute can be well represented by a quadratic formalism over a wide composition range as,

$$\log \gamma_1 = \alpha_{12} X_2^2 \quad \ldots\ldots\ldots\ldots\ldots(1)$$

and

$$\log \gamma_2 = \log \gamma_2^\circ + \alpha_{12}(-2X_2 + X_2^2) \quad \ldots\ldots\ldots(2)$$

where, subscripts 1, 2: solvent and solute, respectively.

The Gibbs–Duhem equation for a binary system can be modified and put in the form

$$\frac{d \log \gamma_1}{d(X_2^2)} = \frac{d \log \gamma_2}{d(X_1^2)} = -\frac{1}{4.605RT} \frac{d^2 G^{xs}}{dX_2^2} \quad \ldots\ldots\ldots\ldots\ldots(3)$$

Darken called the second derivative of the excess free energy with respect to composition ' excess stability ' and studied the behaviour of excess stability in a number of binary metallic alloys. The excess stability function remains reasonably constant within the limits of experimental uncertainity, in the terminal regions extending upto 30 at% solute. In strongly interacting systems the validity of the quadratic formalism is limited to a smaller concentration range.

In the subsequent paper, Darken[2] extended the quadratic formalism to several Fe–C–X ternary systems and observed that this formalism is adequate to represent available data upto solute (X) concentrations of 20 to 30 at%. This communication is aimed at extending the quadratic formalism in a general manner to dilute multicomponent solutions. The thermodynamic consistency of the quadratic formalism for multicomponent systems is examined. Finally the quadratic formalism is compared with the second order interaction parameter representation and the interrelations are discussed.

2. Quadratic Formalism for Multicomponent Solutions

A quadratic equation for the excess integral free energy of a ternary solution for solvent rich composition is[2]

$$\frac{G^{xs}}{2.303RT} = X_2 \log \gamma_2^\circ + X_3 \log \gamma_3^\circ - \alpha_{12} X_2^2 - \alpha_{13} X_3^2$$
$$- (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3 \quad \ldots\ldots\ldots\ldots(4)$$

The corresponding expressions for partial properties or activity coefficients derived using the Gibbs–Duhem equation are,[2]

$$\log \gamma_1 = \alpha_{12} X_2^2 + \alpha_{13} X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3$$
$$\log \gamma_2 = \log \gamma_2^\circ - 2\alpha_{12} X_2 + (\alpha_{23} - \alpha_{12} - \alpha_{13}) X_3$$
$$+ \alpha_{12} X_2^2 + \alpha_{13} X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3$$
$$\log \gamma_3 = \log \gamma_3^\circ - 2\alpha_{13} X_3 + (\alpha_{23} - \alpha_{12} - \alpha_{13}) X_2$$
$$+ \alpha_{12} X_2^2 + \alpha_{13} X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3$$
$$\ldots\ldots\ldots\ldots(5)$$

where, subscript 1: solvent
2, 3: solutes.

Eqs. (5) have been shown by Darken to be thermodynamically consistent, reduce at $X_2 = 0$ or $X_3 = 0$ to an appropriate formalism for a binary solution and

approach at infinite dilution Raoult's law for the solvent. The quadratic representation for the excess integral free energy in a quaternary system for solvent rich compositions is;[2]

$$\frac{G^{xs}}{2.303RT} = X_2 \log \gamma_2^\circ + X_3 \log \gamma_3^\circ + X_4 \log \gamma_4^\circ - \alpha_{12}X_2^2$$

$$-\alpha_{13}X_3^2 - \alpha_{14}X_4^2 - (\alpha_{12}+\alpha_{13}-\alpha_{23})X_2X_3$$

$$-(\alpha_{12}+\alpha_{14}-\alpha_{24})X_2X_4$$

$$-(\alpha_{13}+\alpha_{14}-\alpha_{34})X_3X_4 \quad \text{...............(6)}$$

which is an obvious extension of Eq. (4). On the same lines, quadratic representation of the integral excess Gibbs energy in a dilute multicomponent solution may be written as,

$$\frac{G^{xs}}{2.303RT} = \sum_{i=2}^{m} X_i \log \gamma_i^\circ - \sum_{i<j}^{m} (\alpha_{1i}+\alpha_{1j}-\alpha_{ij})X_iX_j$$

$$-\sum_{i=2}^{m} \alpha_{1i}X_i^2 \quad \text{...............(7)}$$

where, subscript 1: solvent

$\quad\quad\quad\quad\quad i, j$: solutes

$\quad\quad\quad\quad\quad m$: the number of components.

From Eq. (7) one may obtain expressions for the partial excess free energies by means of the general thermodynamic relations for a multicomponent solution at constant T and P.

$$G_p^{xs} = G^{xs} + \sum_{n=2}^{m} (\delta_{pn}-X_n)\frac{\partial G^{xs}}{\partial X_n} \quad \text{...........(8)}$$

where, δ_{pn}: the Kronecker's symbol ($\delta_{pn}=0$ for $p \neq n$ and $\delta_{pn}=1$ for $p=n$) for all values of p from 1 to m.

The relations for the activity coefficients are thus found to be,

$$\log \gamma_1 = \sum_{j<k}^{m} (\alpha_{1j}+\alpha_{1k}-\alpha_{jk})X_jX_k + \sum_{j=2}^{m} \alpha_{1j}X_j^2$$

$$\text{.................(9)}$$

$$\log \gamma_i = \log \gamma_i^\circ - 2\alpha_{1i}X_i - \sum_{\substack{j=2\\j\neq i}}^{m} (\alpha_{1i}+\alpha_{1j}-\alpha_{ij})X_j$$

$$+\sum_{j<k}^{m} (\alpha_{1j}+\alpha_{1k}-\alpha_{jk})X_jX_k + \sum_{j=2}^{m} \alpha_{1j}X_j^2$$

$$\text{.................(10)}$$

Eqs. (9) and (10) reduce to Eqs. (5) for a ternary system and to Eqs. (1) and (2) for a binary system, respectively, under appropriate limiting conditions. Relations (9) and (10) can also be deduced from a different form of the thermodynamic relation

$$G_p^{xs} = G^{xs} + (1-X_p)$$

$$\times\left(\frac{\partial G^{xs}}{\partial X_p}\right)_{T,P,X_n/X_o}\begin{bmatrix}n \neq o \neq p\\n=1...m; \ o=1...m\end{bmatrix}$$

$$\text{.................(11)}$$

for all values of p from 1 to m.

3. Comparison of the Darken's Formalism with the Interaction Parameter Formalism

An expression for the logarithm of the activity coefficients of solutes in terms of the second order interaction parameter representation is[3]

$$\ln \gamma_i = \ln \gamma_i^2 + \varepsilon_i^i X_i + \sum_{\substack{j=2\\j\neq i}}^{m} \varepsilon_i^j X_j + \sum_{j<k}^{m} \rho_i^{jk} X_j X_k$$

$$+\sum_{j=2}^{m} \rho_i^j X_j^2 \quad \text{...............(12)}$$

The convention adopted here for superscripts and subscripts is same as that of Lupis.[3] It has been shown recently[4] that the truncated Maclaurin series for the activity coefficient in ternary and higher order systems is not thermodynamically consistent in its general form. Moreover, if the activity coefficients of all solutes and solvent are expressed by a second order Maclaurin series expansion, then Gibbs–Duhem equation imposes certain relation between the coefficients of the series. For a ternary system these are[4]

$$\varepsilon_2^2 = -2\rho_2^2 = -2\rho_3^2$$

$$\varepsilon_3^3 = -2\rho_3^3 = -2\rho_2^3$$

$$\varepsilon_2^3 = \varepsilon_3^2 = -\rho_2^{23} = -\rho_3^{23} \quad \text{.................(13)}$$

Relations (13) are same as that derived by Schuhmann[5] using a slightly different approach. It is also seen that upon substitution of Eq. (13) into Eq. (12), for a ternary system, Eq. (12) reduces to the form suggested by Pelton and Bale,[6] albeit through an inexact procedure.[4] Comparing Eqs. (10) and (12) we arrive at the following relations:

$$\varepsilon_i^i = -2\rho_i^i = -(2.303)2\alpha_{1i} \quad\quad (i = 2...m)$$

$$\varepsilon_i^j = -\rho_i^{ij} = -(2.303)(\alpha_{1i}+\alpha_{1j}-\alpha_{ij})$$

$$(i, j = 2...m \ \text{and} \ i \neq j)$$

$$\rho_i^{jk} = (2.303)(\alpha_{1j}+\alpha_{1k}-\alpha_{jk})$$

$$(i, j, k = 2...m \ \text{and} \ j \neq k)$$

$$\rho_i^j = (2.303)\alpha_{1j} \quad\quad (i, j = 2...m)$$

$$\text{.................(14)}$$

Eqs. (13) are only a specific case (i.e., applied to a ternary system) of the general relations expressed by Eqs. (14). Substitution of Eqs. (14) in Eq. (12) gives an equation identical to that derived by Pelton and Bale[6] for a multicomponent system. In summary, quadratic formalism is identical to the second order interaction parameter formalism in which interaction parameters are related by Eqs. (14). It is apparent that interaction parameter formalisms other than the second order can not be reconciled with the quadratic formalism.

4. Entropy and Enthalpy Parameters in Quadratic Formalism

The enthalpy and excess entropy functions can also be represented by a quadratic formalism

$$H = \sum_{i=2}^{m} X_i H_i^\circ - \sum_{i<j}^{m} (h_{1i}+h_{1j}-h_{ij})X_iX_j$$

$$-\sum_{i=2}^{m} h_{1i}X_i^2 \quad \text{...............(15)}$$

$$S^{xs} = \sum_{i=2}^{m} X_i S_i^{xs\circ} - \sum_{i<j}^{m}\sum (s_{1i}+s_{1j}-s_{ij})X_iX_j$$
$$- \sum_{i=2}^{m} s_{1i}X_i^2 \quad\quad\quad\quad\quad\quad\text{...............(16)}$$

where, h, s: the enthalpy and entropy parameters that relate to α, respectively.

The corresponding expressions for partial properties of the solvent are given by

$$H_1 = \sum_{j<k}\sum (h_{1j}+h_{1k}-h_{jk})X_jX_k + \sum_{j=2}^{m} h_{1j}X_j^2$$
$$\text{....................(17)}$$

$$S_1^{xs} = \sum_{j<k}\sum (s_{1j}+s_{1k}-s_{jk})X_jX_k + \sum_{j=2}^{m} s_{1j}X_j^2$$
$$\text{....................(18)}$$

and for the solutes

$$H_i = H_i^\circ - 2h_{1i}X_i - \sum_{\substack{j=2\\j\neq i}}^{m} (h_{1i}+h_{1j}-h_{ij})X_j$$
$$+ \sum_{j<k}\sum (h_{1j}+h_{1k}-h_{jk})X_jX_k + \sum_{j=2}^{m} h_{1j}X_j^2$$
$$\text{....................(19)}$$

$$S_i^{xs} = S_i^{xs\circ} - 2s_{1i}X_i - \sum_{\substack{j=2\\j\neq i}}^{m} (s_{1i}+s_{1j}-s_{ij})X_j$$
$$+ \sum_{j<k}\sum (s_{1j}+s_{1k}-s_{jk})X_jX_k + \sum_{j=2}^{m} s_{1j}X_j^2$$
$$\text{....................(20)}$$

There are relations between the free energy, enthalpy and entropy parameters. Since

$$G^{xs} = H - TS^{xs}$$

then

$$\alpha_{no} = \frac{h_{no}}{2.303RT} - \frac{s_{no}}{2.303R} \quad (n\neq o) \quad\text{.........(21)}$$

for all values of n and o from 1 to m. Comparing the quadratic formalism for enthalpy and excess entropy with a second order Maclaurin series representation, we can arrive at relations similar to Eqs. (14). Following the convention of Lupis,[3] the enthalpy correlations are

$$\eta_i^i = -2\lambda_i^i = -(2.303)2h_{1i} \quad\quad (i = 2...m)$$
$$\eta_i^j = -\lambda_i^{ij} = -(2.303)(h_{1i}+h_{1j}-h_{ij})$$
$$\quad\quad\quad\quad (i, j = 2...m \text{ and } i\neq j)$$
$$\lambda_i^{jk} = (2.303)(h_{1j}+h_{1k}-h_{jk})$$
$$\quad\quad\quad\quad (i, j, k = 2...m \text{ and } j\neq k)$$
$$\lambda_i^j = (2.303)h_{1j} \quad\quad\quad (i, j = 2...m)$$
$$\text{....................(22)}$$

where, η, λ: the first and the second order enthalpy interaction coefficients, respectively.[3]

Similarly, the entropy correlations are

$$\sigma_i^i = -2\pi_i^i = -(2.303)2s_{1i} \quad\quad (i = 2...m)$$
$$\sigma_i^j = -\pi_i^{ij} = -(2.303)(s_{1i}+s_{1j}-s_{ij})$$
$$\quad\quad\quad\quad (i, j = 2...m \text{ and } i\neq j)$$
$$\pi_i^{jk} = 2.303(s_{1j}+s_{1k}-s_{jk})$$
$$\quad\quad\quad\quad (i, j, k = 2...m \text{ and } j\neq k)$$
$$\pi_i^j = 2.303s_{1j} \quad\quad\quad (i, j = 2...m)$$
$$\text{....................(23)}$$

where, σ, π: the first and the second order entropy interaction coefficients, respectively.

The enthalpy interaction coefficient can be obtained either through the temperature dependence of the free energy interaction coefficient or independently by calorimetric measurements. The entropy interaction coefficient is determined from the enthalpy and free energy interaction coefficients using Eq. (21).

Jacob and Jeffes[7] have shown that the first order enthalpy and entropy interaction parameters in M–O–X system are related by an empirical expression,

$$\eta_i^j = \tau\sigma_i^j \quad\quad\quad\quad\text{...........(24)}$$

If a self-consistent second order Maclaurin series expansion for the activity coefficient of solute is chosen, then it follows that

$$\lambda_i^j = \tau\pi_i^j \quad\quad\quad\quad\text{...........(25)}$$

If similar relations also hold between the self interaction parameters ($\eta_i^i = \tau\sigma_i^i$), then it can be shown that the enthalpy and entropy parameters of the quadratic formalism are also related,

$$h_{ij} = \tau s_{ij} \quad\quad\quad\quad\text{...........(26)}$$

The characteristic temperature (τ) where the free energy parameters become zero may be expected to vary with the melting point of the solvent although it is difficult to discern such trends because of the uncertainty in the experimental data. The value of the characteristic temperature (τ) has been evaluated as 1 820 K based mainly on data for systems with copper and lead as solvents. For iron as a solvent this characteristic temperature is expected to be $\approx 2\,400$ K. The main utility of this empirical correlation between enthalpy and entropy parameters is in the estimation of free energy parameter at temperatures different from that used in measurement.

5. Thermodynamic Consistency of the Quadratic Formalism

From the fundamental definition, the Gibbs free energy G is a state function and hence its differential is exact. In a mathematical sense the necessary and sufficient condition for exactness is given by Maxwell's relation,

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial n_j}\right) = \frac{\partial}{\partial n_j}\left(\frac{\partial G}{\partial n_i}\right) \quad\text{............(27)}$$

for all values of i and j, where n_i and n_j are the number of moles of components i and j. It has been mentioned earlier[4] that this condition for exactness can be modified and rewritten in terms of the partial property and mole fraction as

$$\frac{\partial\ln\gamma_j}{\partial X_i} - \sum_{k=2}^{m} X_k\frac{\partial\ln\gamma_j}{\partial X_k} = \frac{\partial\ln\gamma_i}{\partial X_j} - \sum_{k=2}^{m} X_k\frac{\partial\ln\gamma_i}{\partial X_k}$$
$$\text{....................(28)}$$

Noncompliance of any formalism to relationship (28) implies that dG is inexact which is thermodynamically inconsistent. It has been mentioned earlier[4] that in

general truncated Maclaurin series for the activity coefficient in ternary and higher order systems does not obey their condition for thermodynamic consistency and hence the integrals are path dependent. They can be made consistent by invoking special relationships between interaction parameters derived from the Gibbs–Duhem equation. Darken's quadratic formalism for ternary system has been shown to satisfy the condition for thermodynamic consistency.[2] It can be shown that the quadratic formalism extended to multicomponent solutions also obeys the condition for thermodynamic consistency, i.e., Eq. (28). Differentiating Eq. (10) with respect to X_j,

$$-\frac{\partial \ln \gamma_i}{\partial X_j} = -(\alpha_{1i} + \alpha_{1j} - \alpha_{ij}) + \sum_{\substack{k=2 \\ k \neq j}}^{m} (\alpha_{1j} + \alpha_{1k} - \alpha_{jk}) X_k$$
$$+ 2\alpha_{1j} X_j \quad\text{.......................................(29)}$$

Similarly, differentiating Eq. (10) with respect to X_k and taking the summation of mole fraction weighted terms

$$\sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_i}{\partial X_k} = -2\alpha_{1i} X_i - \sum_{\substack{k=2 \\ k \neq j}}^{m} (\alpha_{1i} + \alpha_{1k} - \alpha_{ik}) X_k$$
$$+ 2 \sum_{j<k}^{m} (\alpha_{1j} + \alpha_{1k} - \alpha_{jk}) X_j X_k$$
$$+ 2 \sum_{k=2}^{m} \alpha_{1k} X_k^2 \quad\text{........................(30)}$$

Similarly it can be shown that

$$\frac{\partial \ln \gamma_j}{\partial X_i} = -(\alpha_{1j} + \alpha_{1i} - \alpha_{ij}) + \sum_{\substack{k=2 \\ k \neq j}}^{m} (\alpha_{1i} + \alpha_{1k} - \alpha_{ik}) X_k$$
$$+ 2\alpha_{1i} X_i \quad\text{...................................(31)}$$

and

$$\sum_{k=2}^{m} X_k \frac{\partial \ln \gamma_j}{\partial X_k} = -2\alpha_{1j} X_j - \sum_{\substack{k=2 \\ k \neq j}}^{m} (\alpha_{1j} + \alpha_{1k} - \alpha_{jk}) X_k$$
$$+ 2 \sum_{i<k}^{m} (\alpha_{1i} + \alpha_{1k} - \alpha_{ik}) X_i X_k$$
$$+ 2 \sum_{k=2}^{m} \alpha_{1k} X_k^2 \quad\text{........................(32)}$$

Substituting Eq. (29) to Eq. (32), the exactness criteria, i.e., Eq. (28) is satisfied.

6. Advantages of the Quadratic Formalism

In the quadratic formalism, the activity coefficients at infinite dilution and solvent–solute interaction terms are obtainable from individual binary systems, and solute–solute interaction terms are in principle derivable from a single measurement on each of the constituent ternary systems. Hence, when the quadratic formalism fits the data in dilute multicomponent solutions, data management is largely simplified. Further, the quadratic formalism unlike the linear ε formalism is thermodynamically consistent. The quadratic formalism is expected to apply to dilute multicomponent solutions which do not exhibit large positive or negative deviations from ideality. In such systems it provides a valuable procedure for Gibbs–Duhem integration in the terminal regions. The validity of the quadratic formalism to multicomponent solutions can be tested using published data in the literature or by careful new measurements. The published data has been analysed mainly in terms of the interaction parameter formalism and certain bias exists in some of this data. Data compilation on ternary systems by Sigworth et al.[8-10] indicate that the relations $\varepsilon_2^2 = -2\rho_2^2 = -2\rho_3^2$, $\varepsilon_3^3 = -2\rho_3^3 = -2\rho_2^3$, $\varepsilon_2^3 = -\rho_2^{23} = -\rho_3^{23}$ are not generally satisfied. This implies that Darken's quadratic formalism may not have universal applicability. Careful studies are under way to test Darken's quadratic formalism in multicomponent solutions.

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