



Recent developments for molten salt systems in Thermochemica

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ABSTRACT

The modified quasi-chemical model in the quadruplet approximation has been implemented in the open-source equilibrium thermodynamics library Thermochemica, enabling single point equilibrium calculations and sophisticated multi-physics simulations of molten salt nuclear systems. Here, the derivations necessary to obtain the chemical potentials of the quadruplet species required for Gibbs energy minimization are provided. The implementation is verified via code-to-code benchmarking against FactSage. A scheme to increase computational efficiency of multi-physics simulations including Thermochemica is described and its effectiveness for molten salt systems demonstrated. Finally, a multi-physics simulation of a molten salt nuclear fuel system is presented as a demonstration problem: ORIGEN-S is used to calculate the isotopic evolution of a fuel-loaded FLiBe mixture with fission and activation products as Thermochemica predicts the phase evolution and number of moles of Cs in various phases.

1. Introduction

With the recent increase in world-wide interest in Molten Salt (nuclear) Reactor (MSR) designs [1], the need for efficient and accurate chemical thermodynamics calculations involving molten salts has grown rapidly. The MSR concept is being actively explored as a next generation nuclear reactor design in Canada, United States, Europe, and several other nation states in both large scale (e.g., approximately 1000 GWe) and small modular reactor platforms. Molten salts are also used in other engineering applications, including solar technologies. The Modified Quasi-chemical Model (MQM) [2–4] in the Quadruplet Approximation (MQMQA) [5,6] has proven to be an effective model for representing fluoride [7–12] and chloride [8,11–14] salt systems. Use of the MQMQA specifically within the FactSage [15] software in which it was first made available has been extremely popular in recent years [16–21]. Unlike other classes of thermodynamic models that focus on the mixing of constituents, the MQMQA focuses on the mixing of pairs (or quadruplets) of constituents to capture short-range ordering.

As a result of this rapidly growing interest, the MQMQA has been implemented in Thermochemica [22]. Thermochemica offers two features that distinguish it from other software: Thermochemica is a free, open-source library, and Thermochemica may be readily coupled to other software for the purposes of multi-physics simulations. In particular, Thermochemica has a history of use in multi-physics simulations of nuclear fuel materials [23–28]. Thus, implementation of MQMQA in

Thermochemica enables the integration of Thermochemica into multi-physics simulations of MSRs. Due to widespread concerns over possible corrosion of MSR components by the salts themselves [29], thermochemical predictions for these systems are of particularly high importance. Through the use of Thermochemica, designers of MSR systems may be able to predict when corrosion of reactor components and formation of precipitate or gaseous species may occur, and seek combinations of chemistry and operating conditions that minimize these occurrences.

A critical step in implementing the MQMQA into Thermochemica, or any other Gibbs energy minimizer that uses explicit expressions for the chemical potentials, is the derivation of equations to represent the chemical potentials of individual species as input to the Hessian matrix. These equations have not been previously presented in the literature and are not trivial to derive. One objective of this paper is to provide a derivation of these equations, which will be helpful to others in implementing this model into their own programming. Another objective of this work is to demonstrate capabilities in using such calculations in a multi-physics code for subsequent engineering analyses.

In Section 2, the equations required to implement the MQMQA in thermodynamic software are derived. In Section 3, the implementation of these equations in Thermochemica is verified. In Section 4, a method for accelerating multi-physics simulations employing Thermochemica through re-initialization is described. In Section 5 an application of the

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MQMQA in Thermochemica to a multi-physics simulation of a molten salt nuclear fuel system is demonstrated. In Section 6 concepts for improvement and future applications are laid out.

2. Derivation of chemical potentials within the modified quasi-chemical model

Thermochemica [22] is an open-source equilibrium thermodynamics software library that solves for a unique combination of phases and concentrations that minimizes the Gibbs energy of an input system. This is performed using the Gibbs Energy Minimization (GEM) method [30]. The approach of the GEM method is to optimize the system such that the residuals in mass balance equations and the total Gibbs energy are simultaneously minimized, subject to the constraints of the Gibbs Phase Rule and conservation of mass [30,31]. Upon successful optimization of the chemical system, many thermochemical properties are available, including the mass of stable phases, the concentrations of all species in every stable solution phase, the Gibbs energy of the system, and the chemical potentials of all system components and stable species in the system. Some of these quantities may be used directly in the context of multi-physics simulations, while others might feed into parametrizations of necessary thermophysical properties.

The Gibbs energy of a solution phase depends on its composition, and a number of models and parameters have been proposed to model different phases. These models include ideal solution models, models for a single sublattice and models for multiple sublattices (e.g., Compound Energy Formalism (CEF) [32]). Despite the large number of models available to represent the Gibbs energy of a phase, the general representative expression is as follows:

$$G = G^\circ + G^{\text{id}} + G^{\text{ex}} + G^{\text{phys}}, \quad (1)$$

where the Gibbs energy of the phase, G , is a sum of the reference Gibbs energy of its species, G° , which depends only on temperature, hydrostatic pressure and composition of individual species, the ideal mixing term of Gibbs energy, $G^{\text{id}} = -TS^{\text{id}}$, which assumes random mixing of constituents with S^{id} denoting the entropy of mixing, and a term to account for non-ideal mixing energy, G^{ex} . The term G^{phys} captures the various physical phenomena that contribute to the Gibbs energy of the phase (e.g., magnetic contributions), and is not used within the existing MQMQA formalism.

The chemical potential of species i is by definition the partial derivative of the integral Gibbs energy of the system with respect to the number of moles of that species at constant temperature, T , and pressure, P . Mathematically, this is represented as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}, \quad (2)$$

where n_i represents the number of moles of species i . One can obtain an expanded expression for chemical potential of i by substituting Eq. (1) into Eq. (2) above, which gives the following:

$$\mu_i = \underbrace{\left(\frac{\partial G^\circ}{\partial n_i} \right)_{T,P,n_{j \neq i}}}_{\mu_i^\circ} + \underbrace{\left(\frac{\partial G^{\text{id}}}{\partial n_i} \right)_{T,P,n_{j \neq i}}}_{\mu_i^{\text{id}}} + \underbrace{\left(\frac{\partial G^{\text{ex}}}{\partial n_i} \right)_{T,P,n_{j \neq i}}}_{\mu_i^{\text{ex}}}, \quad (3)$$

where the contributions to the integral Gibbs energy are obtained as the product of number of moles of a phase and the respective molar Gibbs energy contribution (i.e., $G^\circ = ng^\circ$, $G^{\text{id}} = ng^{\text{id}}$ and $G^{\text{ex}} = ng^{\text{ex}}$), with g° , g^{id} and g^{ex} denoting the molar reference Gibbs energy, the molar ideal Gibbs energy of mixing and the molar excess Gibbs energy of mixing, respectively. The partial derivative terms are referred to as the partial reference molar Gibbs energy, partial molar ideal Gibbs energy of mixing and partial molar excess Gibbs energy of mixing and are denoted by μ_i° , μ_i^{id} , and μ_i^{ex} respectively.

The MQMQA is a thermodynamic model for treating Short-Range Order (SRO) with two sublattices. The MQMQA is fundamentally different from other classes of thermodynamic models in that the focus

is not on the mixing of chemical species or constituents on a lattice, but rather the mixing of species as quadruplets to capture SRO of both First-Nearest-Neighbors (FNN) and Second-Nearest-Neighbors (SNN) in liquid or solid solutions. The details of the evolution of the modified quasichemical model from pair approximation for species mixing on only one sublattice to the current quadruplet approximation on two sublattices are provided by Pelton et al. [2,3,5], Chartrand et al. [4], and Lambotte et al. [6].

2.1. Gibbs energy of modified quasichemical model phases

The integral Gibbs energy of a solution phase modeled by MQMQA can be expanded in terms of the site fractions of constituents, X_i , equivalent site fractions of constituents, Y_i , FNN pair fractions, $X_{i/k}$, SNN quadruplet fractions, $X_{ij/kl}$, and the molar quantities corresponding to these fractions. As the quadruplets are taken to be independent components of the phase, it is necessary to express all of these quantities in terms of the molar quantities of the quadruplets, $n_{ij/kl}$. In the subscript notation used throughout, a single subscript (i.e. i) indicates a cation or anion constituent, a subscript pair (i/k) indicates a pair consisting of cation constituent i and anion constituent k , and a quartet (ij/kl) indicates a quadruplet composed of cation constituents i and j , and anion constituents k and l . The quadruplet fractions are:

$$X_{ij/kl} = \frac{n_{ij/kl}}{\sum_{ab/xy} n_{ab/xy}}. \quad (4)$$

The molar quantity of a pair i/k is:

$$n_{i/k} = \sum_{ab/xy} n_{ab/xy} \frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{\zeta_{i/k}}, \quad (5)$$

where δ is the Kronecker delta function, and $\zeta_{i/k}$ is the FNN to SNN ratio for the pair i/k . Then, the mole fraction of a pair is:

$$X_{i/k} = \frac{n_{i/k}}{\sum_{a/x} n_{a/x}}. \quad (6)$$

Next are the site molar quantities, n_i . Since the site fractions are specific to each sublattice, the calculation of each is explicitly shown (i.e. n_i^{1st} and n_k^{2nd}). In the following discussion, the distinction will not be carried through, and the convention will be that if a constituent i is on the first sublattice, then X_i is implicitly X_i^{1st} . That said,

$$n_i^{\text{1st}} = \sum_{ab/xy} n_{ab/xy} \left(\frac{\delta_{ai}}{Z_{ab/xy}^a} + \frac{\delta_{bi}}{Z_{ab/xy}^b} \right), \quad (7)$$

where $Z_{ij/kl}^i$ is the coordination number of constituent i within the quadruplet ij/kl , and

$$n_k^{\text{2nd}} = \sum_{ab/xy} n_{ab/xy} \left(\frac{\delta_{xk}}{Z_{ab/xy}^x} + \frac{\delta_{yk}}{Z_{ab/xy}^y} \right). \quad (8)$$

Then, the site fractions are:

$$X_i^{\text{1st}} = \frac{n_i^{\text{1st}}}{\sum_a n_a^{\text{1st}}}, \quad (9)$$

and

$$X_k^{\text{2nd}} = \frac{n_k^{\text{2nd}}}{\sum_x n_x^{\text{2nd}}}. \quad (10)$$

The site-equivalent fractions (Y_i) are calculated similar to the site molar quantities (n_i), and the same convention will be used here to distinguish between sublattices. They are then:

$$Y_i^{\text{1st}} = \sum_{ab/xy} X_{ab/xy} \left(\frac{\delta_{ai} + \delta_{bi}}{2} \right), \quad (11)$$

and

$$Y_k^{\text{2nd}} = \sum_{ab/xy} X_{ab/xy} \left(\frac{\delta_{xk} + \delta_{yk}}{2} \right). \quad (12)$$

The coordination-equivalent fractions (F_i), which are identical to the site-equivalent fractions (Y_i) when all $\xi_{i/k}$ are equal, are defined as [6]:

$$F_i^{1st} = \sum_{a/x} \delta_{ai} X_{a/x}, \quad (13)$$

and

$$F_k^{2nd} = \sum_{a/x} \delta_{xk} X_{a/x}. \quad (14)$$

The reference Gibbs energy term is given as follows:

$$G^\circ = \sum_{ij/kl} n_{ij/kl} g_{ij/kl}^\circ, \quad (15)$$

where $g_{ij/kl}^\circ$ denotes the reference molar Gibbs energy of the quadruplet. The configurational entropy terms can be written as the following:

$$\Delta S = -R \left[\sum_i n_i \ln(X_i) + \sum_{i/k} n_{i/k} \ln \left(\frac{X_{i/k}}{F_i F_k} \right) + \sum_{ij/kl} n_{ij/kl} \ln \left(\frac{X_{ij/kl}}{C_{ij/kl} (X_{i/k} X_{j/l} X_{j/k} X_{i/l})^\phi (Y_i Y_j Y_k Y_l)^\psi} \right) \right], \quad (16)$$

where R is the ideal gas constant, $C_{ij/kl} = (2 - \delta_{ij})(2 - \delta_{kl})$ with δ being the Kronecker delta function, and the exponents ϕ and ψ take the values 1 and 1, or $3/4$ and $1/2$, depending on whether the original or the updated implementation of MQMQA is used [6]. The excess Gibbs energy term takes the following form:

$$G^{ex} = \frac{1}{2} \left[\sum_{ij/kl} n_{ij/kl} \Delta g_{ij/kl} + \sum_{\substack{ij/kl \\ l=k}} \left(\frac{Z_{ij/kl}^k}{2} \sum_{\substack{m \\ m \neq k}} \frac{n_{ij/km}}{Z_{ij/km}^k} \right) \Delta g_{ij/kl} + \sum_{\substack{ij/kl \\ j=l}} \left(\frac{Z_{ij/kl}^l}{2} \sum_{\substack{m \\ m \neq l}} \frac{n_{im/kl}}{Z_{im/kl}^l} \right) \Delta g_{ij/kl} \right]. \quad (17)$$

In the preceding expressions, sums over i are for all constituents, sums over i/k are for all FNN pairs, and sums over ij/kl are for all FNN quadruplets. The empirical mixing parameter used to fit the Gibbs energy of formation of quadruplets, $\Delta g_{ij/kl}$, can take a variety of forms, and indeed even be composed of many of these forms. Because each $\Delta g_{ij/kl}$ contains an unknown number (possibly zero) of terms of various forms, which eventually will be summed, it is convenient to handle each of these terms independently. It should be noted that by definition for quadruplets with $i = j$ and $k = l$, the excess mixing energy is necessarily zero (as no mixing is occurring). For all other quadruplets:

$$\Delta g_{ij/kl} = \sum_{\alpha=1}^{N_{ij/kl}^{ex}} \Delta g_{ij/kl,\alpha}, \quad (18)$$

where $N_{ij/kl}^{ex}$ is the number of excess energy terms corresponding to the ij/kl quadruplet.

As described by Pelton [33], the calculation of excess mixing energy terms within the MQMQA depends on the symmetry of the ternary subsystems. These calculations are aided by the use of the variables $\xi_{ij/k}$ and $\chi_{ij/kk}$. They have been generalized to allow for the existence in the system of multiple constituents on both sublattices and to specify which of these constituents the mixing term corresponds to. $\xi_{ij/k}$ is defined as follows:

$$\xi_{ij/k} = \sum_{a=\{i,v\}} Y_{a/k}, \quad (19)$$

where v represents all constituents that form asymmetrical $i - j - v$ ternary subsystems in which j is the asymmetric constituent. $Y_{i/k}$ is

a modification of Y_i from Eq. (11) such that only contributions from quadruplets containing species k on the second sublattice are included, such that:

$$Y_{i/k} = \sum_{ab/xy} X_{ab/xy} \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right). \quad (20)$$

$\chi_{ij/kk}$ is defined as follows in the original implementation [5]:

$$\begin{aligned} \chi_{ij/kk} &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} X_{ab/kk}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} X_{ab/kk}} \\ &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} n_{ab/kk}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} n_{ab/kk}}, \end{aligned} \quad (21)$$

or in the updated implementation [6,33]:

$$\begin{aligned} \chi_{ij/kk} &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} \sum_x \sum_y \frac{\delta_{kx} + \delta_{ky}}{2} X_{ab/xy}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} \sum_x \sum_y \frac{\delta_{kx} + \delta_{ky}}{2} X_{ab/xy}} \\ &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} \sum_x \sum_y \frac{\delta_{kx} + \delta_{ky}}{2} n_{ab/xy}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} \sum_x \sum_y \frac{\delta_{kx} + \delta_{ky}}{2} n_{ab/xy}}, \end{aligned} \quad (22)$$

where γ represents all constituents that form asymmetrical $i - j - \gamma$ ternary subsystems in which i is the asymmetric constituent. The sums over x and y are for all constituents on the second sublattice. These equations can be reversed to apply to the second sublattice, but for the sake of brevity from here on only mixing on the first sublattice will be shown explicitly. In Eq. (21), it can be observed that because the numerator and denominator involve the same powers of $X_{ij/kl}$, the mole fractions can be replaced with the molar quantities.

There are numerous possibilities for the form of each $\Delta g_{ij/kl,\alpha}$. These include binary mixing terms proportional to the quadruplet fractions:

$$\Delta g_{ij/kk,\alpha} = g_{ij/kk,\alpha} \cdot \chi_{ij/kk}^{p_\alpha} \chi_{ji/kk}^{q_\alpha}, \quad (23)$$

binary mixing proportional to equivalent site fractions:

$$\Delta g_{ij/kk,\alpha} = g_{ij/kk,\alpha} \cdot \frac{\xi_{ij/k}^{p_\alpha} \xi_{ji/k}^{q_\alpha}}{(\xi_{ij/k} + \xi_{ji/k})^{p_\alpha + q_\alpha}}, \quad (24)$$

ternary mixing proportional to the quadruplet fractions:

$$\Delta g_{ij(m)/kk,\alpha} = g_{ij(m)/kk,\alpha} \cdot \chi_{ij/kk}^{p_\alpha} \chi_{ji/kk}^{q_\alpha} \cdot \begin{cases} \left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_\alpha - 1} & m \in \gamma \\ \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha - 1} & m \in v \\ Y_{m/k} \left(1 - \xi_{ij/k} - \xi_{ji/k} \right)^{r_\alpha - 1} & m \notin \{v, \gamma\}, \end{cases} \quad (25)$$

and ternary mixing proportional to equivalent site fractions:

$$\begin{aligned} \Delta g_{ij(m)/kk,\alpha} &= g_{ij(m)/kk,\alpha} \cdot \frac{\xi_{ij/k}^{p_\alpha} \xi_{ji/k}^{q_\alpha}}{(\xi_{ij/k} + \xi_{ji/k})^{p_\alpha + q_\alpha}} \\ &\cdot \begin{cases} \left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_\alpha - 1} & m \in \gamma \\ \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha - 1} & m \in v \\ Y_{m/k} \left(1 - \xi_{ij/k} - \xi_{ji/k} \right)^{r_\alpha - 1} & m \notin \{v, \gamma\}, \end{cases} \end{aligned} \quad (26)$$

where in the above equations p_α , q_α , and r_α are integer exponents chosen for the excess mixing term α .

In the types of mixing terms described in Eqs. (23)–(26), there is a restriction of having only one constituent involved on either the first or second sublattice. Expressions for mixing on the first sublattice are shown. Note that the terms preceding the cases in Eqs. (25) and (26) correspond to Eqs. (23) and (24), and that the terms within the cases are identical for the two forms of ternary mixing. The cases $m \in \gamma$, $m \in v$, and $m \notin \{v, \gamma\}$ correspond to the ternary system $i - j - m$ being

asymmetric with i as the asymmetric constituent, asymmetric with j as the asymmetric constituent, and either asymmetric with m as the asymmetric constituent or symmetric, respectively. m cannot be equal to either of i and j , as this would not indicate a ternary subsystem.

2.2. Derivation of chemical potential equations

In the MQMQA, the chemical potentials are defined as partial derivatives in terms of the molar quantities of the various quadruplets (analogous to the compound end members in the CEF). Following the procedure employed to compute the Gibbs energies, the chemical potentials are computed as sums of derivatives of the various energetic contributions:

$$\begin{aligned}\mu_{ij/kl} &= \left(\frac{\partial G}{\partial n_{ij/kl}} \right)_{T, P, n_{(ab/xy) \neq (ij/kl)}} \\ &= \left(\frac{\partial G^\circ}{\partial n_{ij/kl}} - T \frac{\partial \Delta S}{\partial n_{ij/kl}} + \frac{\partial G^{\text{ex}}}{\partial n_{ij/kl}} \right)_{T, P, n_{(ab/xy) \neq (ij/kl)}}.\end{aligned}\quad (27)$$

The following sub-sections will derive each of the terms in Eq. (27).

2.2.1. Derivation of the reference Gibbs energy and entropic contributions to chemical potential equations

The partial molar reference Gibbs energy is defined as follows:

$$\frac{\partial G^\circ}{\partial n_{ij/kl}} = g_{ij/kl}^\circ. \quad (28)$$

The entropic contributions to chemical potentials are greatly simplified by the cancellation of the derivatives of the terms within logarithms, which results in:

$$\begin{aligned}\frac{\partial \Delta S}{\partial n_{ij/kl}} &= R \left[\sum_m \frac{\partial n_m}{\partial n_{ij/kl}} \ln(X_m) + \sum_{m/z} \frac{\partial n_{m/z}}{\partial n_{ij/kl}} \ln \left(\frac{X_{m/z}}{F_m F_z} \right) \right. \\ &\quad \left. + \ln \left(\frac{X_{ij/kl}}{C_{ij/kl}(X_{i/k} X_{i/l} X_{j/k} X_{j/l})^\phi / (Y_i Y_j Y_k Y_l)^\psi} \right) \right],\end{aligned}\quad (29)$$

where the sum over m is over all constituents, and the sum over m/z is over all pairs. This leaves only the values of the partial derivatives $\frac{\partial n_m}{\partial n_{ij/kl}}$ and $\frac{\partial n_{m/z}}{\partial n_{ij/kl}}$ to be determined as follows:

$$\frac{\partial n_m}{\partial n_{ij/kl}} = \frac{\delta_{im}}{Z_{ij/kl}^i} + \frac{\delta_{jm}}{Z_{ij/kl}^j} + \frac{\delta_{km}}{Z_{ij/kl}^k} + \frac{\delta_{lm}}{Z_{ij/kl}^l}. \quad (30)$$

While the previous expression is general, it is worth noting that m can never be equal to i or j and k or l at the same time, as the constituent is on either the first sublattice or the second. Finally,

$$\frac{\partial n_{m/z}}{\partial n_{ij/kl}} = \frac{(\delta_{im} + \delta_{jm})(\delta_{kz} + \delta_{lz})}{\zeta_{m/z}}, \quad (31)$$

where $\zeta_{m/z}$ is the ratio of FNN to SNN for the FNN pair m/z .

2.2.2. Derivation of the partial molar excess Gibbs energy contribution to chemical potential

Due to the dependence of excess mixing Gibbs energy terms on the mole fractions of phase components, the derivative of each term with respect to molar amounts of all quadruplets are non-zero, unless if all exponents are zero. This results in many cases for the derivatives, as within each form there are cases for the quadruplets explicitly involved in the mixing, and for the rest that are implicitly involved. Fortunately, as will be shown, these derivatives can be written compactly in terms of the excess mixing energies themselves. It is crucial not to forget the product rule resulting from Eq. (17), in which molar quantities are

multiplied by the sums of individual excess mixing terms:

$$\begin{aligned}\frac{\partial G^{\text{ex}}}{\partial n_{ab/xy}} &= \frac{1}{2} \left[\sum_{ij/kl} \left\{ \frac{\partial n_{ij/kl}}{\partial n_{ab/xy}} \Delta g_{ij/kl} + n_{ij/kl} \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right. \\ &\quad + \sum_{\substack{ij/kl \\ l=k}} \left\{ \frac{Z_{ij/kl}^k}{2} \sum_{m \neq k} \frac{\frac{\partial n_{ij/km}}{\partial n_{ab/xy}}}{Z_{ij/km}^k} \Delta g_{ij/kl} \right. \\ &\quad + \left. \left. \left(\frac{Z_{ij/kl}^k}{2} \sum_{m \neq k} \frac{n_{ij/km}}{Z_{ij/km}^k} \right) \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right. \\ &\quad + \sum_{\substack{ij/kl \\ j=i}} \left\{ \frac{Z_{ij/kl}^i}{2} \sum_{m \neq i} \frac{\frac{\partial n_{im/kl}}{\partial n_{ab/xy}}}{Z_{im/kl}^i} \Delta g_{ij/kl} \right. \\ &\quad + \left. \left. \left(\frac{Z_{ij/kl}^i}{2} \sum_{m \neq i} \frac{n_{im/kl}}{Z_{im/kl}^i} \right) \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right].\end{aligned}\quad (32)$$

$\frac{\partial n_{ij/kl}}{\partial n_{ab/xy}}$ is equal to 1 if $i = a$, $j = b$, $k = x$, and $l = y$, and is 0 otherwise. Thus, the foregoing expression simplifies to the following:

$$\begin{aligned}\frac{\partial G^{\text{ex}}}{\partial n_{ab/xy}} &= \frac{1}{2} \left[\Delta g_{ab/xy} + \sum_{ij/kl} \left\{ n_{ij/kl} \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right. \\ &\quad + \left(\frac{Z_{ab/xx}^x}{2Z_{ab/xy}^x} + \frac{Z_{ab/yy}^y}{2Z_{ab/xy}^y} \right) \Delta g_{ab/xy} \\ &\quad + \sum_{\substack{ij/kl \\ l=k}} \left\{ \frac{Z_{ij/kl}^k}{2} \sum_{m \neq k} \frac{n_{ij/km}}{Z_{ij/km}^k} \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \\ &\quad + \left(\frac{Z_{aa/xy}^a}{2Z_{ab/xy}^a} + \frac{Z_{bb/xy}^b}{2Z_{ab/xy}^b} \right) \Delta g_{ab/xy} \\ &\quad + \sum_{\substack{ij/kl \\ j=i}} \left\{ \frac{Z_{ij/kl}^i}{2} \sum_{m \neq i} \frac{n_{im/kl}}{Z_{im/kl}^i} \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right].\end{aligned}\quad (33)$$

By substituting Eq. (18) into Eq. (33), $\Delta g_{ij/kl}$ can be replaced by $\sum_{\alpha=1}^{N_{ij/kl}^{\text{ex}}} \Delta g_{ij/kl, \alpha}$. Thus, in all cases, the quantity of interest remains $\frac{\partial \Delta g_{ij/kl, \alpha}}{\partial n_{ab/xy}}$. The possible forms for $\Delta g_{ij/kl, \alpha}$ will be approached in the same order as before. Starting with binary mixing based on quadruplet fractions:

$$\begin{aligned}\frac{\partial (\Delta g_{ij/kk, \alpha})}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij/kk, \alpha}}{\sum_{cd/vw} n_{cd/vw}} \cdot \frac{\delta_{xk} \delta_{yk}}{\sum_{c=\{i,j,v,\gamma\}} \sum_{d=\{i,j,v,\gamma\}} X_{cd/kk}} \\ &\quad \times \left[\frac{(\sum_{e=i,v} \delta_{ae}) (\sum_{e=i,v} \delta_{be}) p_\alpha}{X_{ij/kk}} \right. \\ &\quad + \frac{(\sum_{e=j,\gamma} \delta_{ae}) (\sum_{e=j,\gamma} \delta_{be}) q_\alpha}{X_{ji/kk}} \\ &\quad - \left(\sum_{e=i,v} \delta_{ae} + \sum_{e=j,\gamma} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} + \sum_{e=j,\gamma} \delta_{be} \right) \\ &\quad \left. \times (p_\alpha + q_\alpha) \right].\end{aligned}\quad (34)$$

In these equations, advantage has been taken of the equal powers of the mole fractions $X_{ij/kl}$ terms in the numerator and denominator to transform these to the molar quantities $n_{ij/kl}$ prior to differentiation.

Eq. (34) is convenient for computational purposes because the derivative of the excess energy term can be expressed relatively compactly in terms of the excess energy term itself. Furthermore, all quantities can be written in terms of $X_{ij/kl}$ except the denominator of the leading fraction, which will cancel with a similar term in Eq. (33).

Next, one can apply the same procedure to binary mixing based on equivalent site fractions:

$$\begin{aligned} \frac{\partial(\Delta g_{ij/kk,\alpha})}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \left[\left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\ &\quad \times \left(\frac{p_\alpha}{\xi_{ij/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \\ &\quad + \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \\ &\quad \left. \times \left(\frac{q_\alpha}{\xi_{ji/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \right], \end{aligned} \quad (35)$$

which has similar properties to Eq. (34).

As shown in Eqs. (25) and (26), the ternary mixing terms include three possible cases. To compute the derivatives of Eqs. (25) and (26), one must first differentiate these three cases. First, the case in which $m \in \gamma$ results in:

$$\begin{aligned} \frac{\partial}{\partial n_{ab/xy}} &\left[\left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_\alpha - 1} \right] \\ &= \left(\frac{1}{\sum_{cd/vw} n_{cd/vw}} \right) \left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_\alpha - 1} \\ &\quad \cdot \left[\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right. \\ &\quad - \left(\frac{r_\alpha - 1}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\ &\quad \left. \left. - Y_{j/k} \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right\} \right] \end{aligned} \quad (36)$$

Similarly, the case in which $m \in v$ results in:

$$\begin{aligned} \frac{\partial}{\partial n_{ab/xy}} &\left[\left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha - 1} \right] \\ &= \left(\frac{1}{\sum_{cd/vw} n_{cd/vw}} \right) \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha - 1} \\ &\quad \cdot \left[\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right. \\ &\quad - \left(\frac{r_\alpha - 1}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\ &\quad \left. \left. - Y_{i/k} \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right\} \right] \end{aligned} \quad (37)$$

The case in which $m \notin \{v, \gamma\}$ results in:

$$\begin{aligned} \frac{\partial}{\partial n_{ab/xy}} &\left[Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_\alpha - 1} \right] = \left(\frac{Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_\alpha - 1}}{\sum_{cd/vw} n_{cd/vw}} \right) \\ &\quad \cdot \left[-(r_\alpha) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) \right. \\ &\quad + (r_\alpha - 1) \{ 1 - \xi_{ij/k} - \xi_{ji/k} \}^{-1} \\ &\quad \cdot \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\ &\quad \left. \left. - \sum_{e=\{j,\gamma\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \right] \end{aligned} \quad (38)$$

With all the necessary pieces in place, the derivatives for ternary excess energy terms can be formed by combining Eqs. (36), (37), and (38) with Eq. (34) (for the quadruplet fraction formulation) and with Eq. (35) (for the site fraction formulation). Taking the quadruplet fraction case first: Eq. (37) is given in Box I where the cases in the last term were described below equation (26). In the second line of Eq. (39), the term $\delta_{xk}\delta_{yk}$ is replaced with $\frac{1}{2}(\delta_{xk} + \delta_{yk})$ for the updated implementation of MQMQA [6,33]. Finally, the site fraction case: Eq. (38) is given in Box II.

The equations presented here are in a form suitable for direct implementation into software, and have been incorporated in Thermochemica in as similar a manner as is possible within the Fortran language. This is intended to enhance readability of the Thermochemica source code to enable verification, modification, use, and comparison with other software in which the MQMQA is implemented. In the following sections, we will demonstrate verification, modification, and use of the MQMQA in Thermochemica.

$$\begin{aligned}
\frac{\partial \Delta g_{ij(m)/kk,\alpha}}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij(m)/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \\
&\cdot \left[\frac{\delta_{xk} \delta_{yk}}{\sum_{e=\{i,j,v,\gamma\}} \sum_{d=\{i,j,v,\gamma\}} X_{cd/kk}} \left[\frac{(\sum_{e=i,v} \delta_{ae}) (\sum_{e=i,v} \delta_{be}) p_\alpha}{\chi_{ij/kk}} + \frac{(\sum_{e=j,\gamma} \delta_{ae}) (\sum_{e=j,\gamma} \delta_{be}) q_\alpha}{\chi_{ji/kk}} \right. \right. \\
&\quad \left. \left. - \left(\left(\sum_{e=i,v} \delta_{ae} \right) + \left(\sum_{e=j,\gamma} \delta_{ae} \right) \right) \left(\left(\sum_{e=i,v} \delta_{be} \right) + \left(\sum_{e=j,\gamma} \delta_{be} \right) \right) (p_\alpha + q_\alpha) \right] \right. \\
&\quad \left. + \left\{ \begin{aligned} &\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \\ &- \left(\frac{r_\alpha - 1}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{j/k} \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right\} \quad m \in \gamma \\ &\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \\ &- \left(\frac{r_\alpha - 1}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{i/k} \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right\} \quad m \in v \\ &- (r_\alpha) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) + (r_\alpha - 1) \{ 1 - \xi_{ij} - \xi_{ji} \}^{-1} \\ &\cdot \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) - \sum_{e=\{j,\gamma\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \quad m \notin \{v, \gamma\} \end{aligned} \right\} \quad \left. \right\} \quad (39)
\end{aligned}$$

Box I.

$$\begin{aligned}
\frac{\partial \Delta g_{ij(m)/kk,\alpha}}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij(m)/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \\
&\cdot \left[\left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{p_\alpha}{\xi_{ij/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \right. \\
&\quad \left. + \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{q_\alpha}{\xi_{ji/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \right. \\
&\quad \left. + \left\{ \begin{aligned} &\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \\ &- \left(\frac{r_\alpha - 1}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{j/k} \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right\} \quad m \in \gamma \\ &\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \\ &- \left(\frac{r_\alpha - 1}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{i/k} \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right\} \quad m \in v \\ &- (r_\alpha) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) + (r_\alpha - 1) \{ 1 - \xi_{ij} - \xi_{ji} \}^{-1} \\ &\cdot \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) - \sum_{e=\{j,\gamma\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \quad m \notin \{v, \gamma\} \end{aligned} \right\} \quad \left. \right\} \quad (40)
\end{aligned}$$

Box II.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

A.1. Extended derivations

Some steps omitted from the derivations in the main text are included below for curious readers.

Eq. (34):

$$\begin{aligned}
 \frac{\partial(\Delta g_{ij/kk,a})}{\partial n_{ab/xy}} &= g_{ij/kk,a} \frac{\partial}{\partial n_{ab/xy}} \left[\chi_{ij/kk}^{p_a} \chi_{ji/kk}^{q_a} \right] \\
 &= g_{ij/kk,a} \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} X_{cd/kk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} X_{cd/kk}} \right)^{p_a} \right. \\
 &\quad \left. \times \left(\frac{\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} X_{cd/kk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} X_{cd/kk}} \right)^{q_a} \right] \\
 &= g_{ij/kk,a} \frac{\partial}{\partial n_{ab/xy}} \left[\frac{(\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} n_{cd/kk})^{p_a} (\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} n_{cd/kk})^{q_a}}{(\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk})^{p_a+q_a}} \right] \\
 &= g_{ij/kk,a} \delta_{xk} \delta_{yk} \left[\frac{(\sum_{e=\{i,v\}} \delta_{ae}) (\sum_{e=\{i,v\}} \delta_{be}) p_a}{\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} n_{cd/kk}} + \frac{(\sum_{e=\{j,y\}} \delta_{ae}) (\sum_{e=\{j,y\}} \delta_{be}) q_a}{\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} n_{cd/kk}} \right. \\
 &\quad \left. - \frac{(\sum_{e=\{i,v\}} \delta_{ae} + \sum_{e=\{j,y\}} \delta_{ae}) (\sum_{e=\{i,v\}} \delta_{be} + \sum_{e=\{j,y\}} \delta_{be}) (p_a + q_a)}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk}} \right] \\
 &\quad \cdot \left[\frac{(\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} n_{cd/kk})^{p_a} (\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} n_{cd/kk})^{q_a}}{(\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk})^{p_a+q_a}} \right] \\
 &= \Delta g_{ij/kk,a} \frac{\delta_{xk} \delta_{yk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk}} \left[\frac{(\sum_{e=\{i,v\}} \delta_{ae}) (\sum_{e=\{i,v\}} \delta_{be}) p_a}{\chi_{ij/kk}} \right. \\
 &\quad \left. + \frac{(\sum_{e=\{j,y\}} \delta_{ae}) (\sum_{e=\{j,y\}} \delta_{be}) q_a}{\chi_{ji/kk}} - \left(\sum_{e=\{i,v\}} \delta_{ae} + \sum_{e=\{j,y\}} \delta_{ae} \right) \right. \\
 &\quad \left. \times \left(\sum_{e=\{i,v\}} \delta_{be} + \sum_{e=\{j,y\}} \delta_{be} \right) (p_a + q_a) \right] \\
 &= \frac{\Delta g_{ij/kk,a}}{\sum_{cd/vw} n_{cd/vw}} \cdot \frac{\delta_{xk} \delta_{yk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} X_{cd/kk}} \left[\frac{(\sum_{e=\{i,v\}} \delta_{ae}) (\sum_{e=\{i,v\}} \delta_{be}) p_a}{\chi_{ij/kk}} \right. \\
 &\quad \left. + \frac{(\sum_{e=\{j,y\}} \delta_{ae}) (\sum_{e=\{j,y\}} \delta_{be}) q_a}{\chi_{ji/kk}} - \left(\sum_{e=\{i,v\}} \delta_{ae} + \sum_{e=\{j,y\}} \delta_{ae} \right) \right. \\
 &\quad \left. \times \left(\sum_{e=\{i,v\}} \delta_{be} + \sum_{e=\{j,y\}} \delta_{be} \right) (p_a + q_a) \right].
 \end{aligned} \tag{A.1}$$

Eq. (35) is given in Box III.

Eq. (36) is given in Box IV.

Eq. (38):

$$\begin{aligned}
 &\frac{\partial}{\partial n_{ab/xy}} \left[Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_a-1} \right] \\
 &= \frac{\partial}{\partial n_{ab/xy}} \left[Y_{m/k} \left(1 - \sum_{e=\{i,v\}} Y_{e/k} - \sum_{e=\{j,y\}} Y_{e/k} \right)^{r_a-1} \right] \\
 &= \frac{\partial}{\partial n_{ab/xy}} \left[\left(\sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{cm} + \delta_{dm})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right. \\
 &\quad \left\{ 1 - \left(\sum_{e=\{i,v\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right. \\
 &\quad \left. \left. - \left(\sum_{e=\{j,y\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right\}^{r_a-1} \right] \\
 &= \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{1}{\sum_{cd/vw} n_{cd/vw}} \right)^{r_a} \left(\sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{cm} + \delta_{dm})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right. \\
 &\quad \left\{ \sum_{cd/vw} n_{cd/vw} - \left(\sum_{e=\{i,v\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right. \\
 &\quad \left. \left. - \left(\sum_{e=\{j,y\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right\}^{r_a-1} \right] \\
 &= \left(\frac{Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_a-1}}{\sum_{cd/vw} n_{cd/vw}} \right) \\
 &\quad \cdot \left[-(r_a) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) \right. \\
 &\quad \left. + (r_a - 1) \{ 1 - \xi_{ij} - \xi_{ji} \}^{-1} \right. \\
 &\quad \cdot \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\
 &\quad \left. \left. - \sum_{e=\{j,y\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \right]
 \end{aligned} \tag{A.4}$$

Appendix B. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.calphad.2021.102341>.

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