



## Corrigendum

## Corrigendum to “The thermochemistry library Thermochemica”

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## ABSTRACT

The CALPHAD method has been highly relied upon for material design and development and a number of software packages have been developed for computing thermodynamic equilibrium. While Gibbs Energy Minimisation (GEM) has been the most commonly used algorithm for thermodynamic equilibrium calculations, an alternative technique namely Partitioning of Gibbs Energy Minimisation (PGE) was advanced and applied to the thermochemistry library Thermochemica due to some of its numerical advantages. The PGE approach, however, has considerable convergence issues when applied to highly non-ideal solution phases and therefore was eventually abandoned in Thermochemica. This corrigendum illustrates the convergence issues and their underlying cause with the aim of informing the readers about the reasoning for adopting GEM in place of PGE in Thermochemica and may help their own decision making in selecting an algorithm for their own software.

## 1. Introduction

Recent trends in material design and development have relied heavily on the CALPHAD method [1] and over the years a number of software packages have been developed for computing thermodynamic equilibrium, such as Thermo-Calc [2], FactSage [3], PANDAT [4], pyCalphad [5], OpenCalphad [6], Thermochemica [7], Yellowjacket [8], etc. While most thermochemical equilibrium solvers rely on the Gibbs Energy Minimisation (GEM) approach, originally developed by White et al. [9], Piro et al. advanced a numerical procedure called the Partitioning of Gibbs Energy (PGE) in Thermochemica, which built upon the concepts presented by White [10] in combination with that of Eriksson and Thompson [11]. In initial developments of Thermochemica, the PGE method was applied in place of the GEM method due to some numerical advantages that improved the rate of convergence and reduced numerical instabilities for some applications. These advantages include the fact that PGE does not require any numerical dampening to ensure that the mole fractions of the various solution species remain positive as compared to GEM where numerical dampening becomes necessary. This issue will become clearer in the next section. GEM also requires additional corrections to be applied in order to improve the estimates of mole fractions of dilute species. While such corrections can compromise the mass balance constraints in GEM, they are inherently satisfied in PGE, thereby simplifying the numerical process.

Despite its numerical advantages, a significant challenge is experienced when PGE is applied to a broader range of applications that results in considerable convergence issues. Ultimately, the PGE method was abandoned in Thermochemica in favour of the more widely used GEM technique, which offers greater robustness over a wide range of applications. This corrigendum is intended to better inform the readers about the reasoning behind adopting the GEM method in place of PGE, which may help their own decision making in developing their own software. In the current context, for the sake of simplicity, the discussion will focus on species in single-sublattice phases. However, the concepts readily apply to the compound end members and/or quadruplets in multi-sublattice phases.

## 2. Discussion

From a theoretical point view, both GEM and PGE methods should yield the same set of predictions of thermodynamic equilibria: a unique combination of phases and species that are stable in a closed isothermal-isobaric system of fixed composition. The distinction between GEM and PGE lies not in the mathematical content of the equilibrium conditions but rather in the numerical algorithms adopted to solve the problem. At a high level, GEM is an optimisation method, whereas the PGE approach is based on finding the roots of a system of nonlinear equations [12]. To highlight the differences between the two approaches, the conditions for

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thermodynamic equilibrium are first summarized:

1. The conservation of mass must be satisfied:

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_j} x_{i(\lambda)} \nu_{ij} + \sum_{\omega=1}^{\Omega} n_{\omega} \nu_{\omega j}. \quad (1)$$

where  $b_j$  denotes the molar amount of component  $j$  in the system<sup>1</sup>,  $n_{\lambda}$  and  $n_{\omega}$  are the molar amounts of solution phase  $\lambda$  and stoichiometric phase  $\omega$ , respectively.  $x_{i(\lambda)}$  represents the mole fraction of species  $i$  in solution phase  $\lambda$ , and  $\nu_{ij}$  and  $\nu_{\omega j}$  are the stoichiometry coefficients of component  $j$  in species  $i$  and stoichiometric phase  $\omega$ , respectively. Note that this equation also applies to ionic charge to ensure charge neutrality constraints are respected.

2. The Gibbs phase rule must be respected:

$$F = C - \Phi + 2 - \Xi. \quad (2)$$

where  $F$  denotes the degree of freedom of the system,  $C$  represents the number of system components and  $\Phi = \lambda + \Omega$  is the number of phases present at equilibrium.  $\Xi$  represents the number of ionic phases<sup>2</sup>. Under isothermal-isobaric conditions, the Gibbs phase rule is reduced to  $F = C - \Phi - \Xi$ , where  $F \geq 0$ .

3. The Gibbs energy of the system must be at a global minimum. The *necessary condition* corresponding to a local minimum requires that the chemical potentials of any species must be represented by a linear function of the system component potentials as [12–14]:

$$\tilde{\mu}_{i(\lambda)} = \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j, \quad (3)$$

where  $\tilde{\mu}_{i(\lambda)}$  represents the dimensionless chemical potential of species  $i$  and  $\tilde{\Gamma}_j$  represents the dimensionless chemical potential<sup>3</sup> of component  $j$ . The *sufficient condition* for global minimum requires that all the metastable phases abide by the following condition [15–17]:

$$\pi_{\lambda} = \min_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \left( \mu_{i(\lambda)} - \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) \geq 0, \quad (4)$$

that is, the driving force of all the phases believed to be metastable must be positive and all stable phases are zero.

In addition to the above conditions, the following constraints must be respected:

- A. The number of moles of any phase cannot be negative.
- B. The sum of mole fractions of all species in a solution phase must equal unity.

It must be mentioned that both GEM and PGE are methods for computing local minima and to compute the global minimum, they must be coupled with a global optimisation routine, some of which have been analysed by Piro and Simunovic [17].

The fundamental premise of GEM is to define the quantities of all species and phases as the *independent* variables, and their corresponding chemical potentials as *dependent* variables (i.e.,  $\mu_i = f(\mathbf{x})$ ). In contrast,

the PGE method defines the chemical potentials as *independent* variables, and the quantities of species and phases as the *dependent* variables (i.e.,  $\mathbf{x}_i = f(\boldsymbol{\mu})$ ). In GEM, the estimated quantities of all species and phases are iteratively altered to progressively minimize the Gibbs energy of the system. In other words, the GEM approach optimises equilibrium conditions 1 and 3 while constraining equilibrium condition 2 [9,18,19].

Thus, the mass balance residuals and residuals of chemical potentials of each phase with respect to the system components are simultaneously minimised in GEM [7]. The number of moles of each solution species is updated with a linear function, which is then used to compute the conjugate chemical potential terms. One must often dampen this calculation to prevent the computation of the logarithm of a negative number. In contrast, the PGE method defines the chemical potentials of all species and phases by a set chemical potentials of the system components, which are then used to compute the mole fractions of individual species and iteratively attempts to satisfy the mass balance equations in Eq. (1). Thus, PGE constrains equilibrium conditions 2 and 3 while iteratively satisfying equilibrium condition 1 [7]. Furthermore, since the PGE method defines the mole fraction as an exponential function, rather than a linear function involving the natural logarithm, it will always be positive as long as the chemical potentials are real. This feature reduces the need for numerical dampening in PGE.

The distinguishing feature of PGE is in solving a system of non-linear equations to find the roots of the mass balance equations, which requires representing the mole fraction of any species as an exponential function involving the system component potentials. One can formulate an explicit function for species in an ideal solution phase; however, for non-ideal solution phases requiring an excess Gibbs energy of mixing contribution, this is not always a straightforward mathematical operation. The Gibbs energy of a non-ideal solution phase is generally given as:

$$G_{\lambda} = G_{\lambda}^{\circ} + G_{\lambda}^{\text{id}} + G_{\lambda}^{\text{ex}}, \quad (5)$$

where  $G_{\lambda}$  is the Gibbs energy of the solution phase  $\lambda$  and the superscripts  $\circ$ , id and ex denote the reference, ideal mixing and excess mixing contributions, respectively. The chemical potential of species  $i$  in solution phase  $\lambda$  is generally given as:

$$\mu_{i(\lambda)} = \left( \frac{\partial G_{\lambda}}{\partial n_{i(\lambda)}} \right)_{T,P,n_{j \neq i}} \quad (6)$$

For a species in an ideal solution phase, the reference and ideal mixing contributions result in linear contributions to the chemical potentials, yielding:

$$\tilde{\mu}_{i(\lambda)} = \tilde{\mu}_{i(\lambda)}^{\circ} + \ln(x_{i(\lambda)}) \quad (7)$$

Recall that  $\tilde{\mu}_{i(\lambda)}$  represents the dimensionless chemical potential, which is why  $RT$  is not used in the foregoing equation.

Substituting Eq. 3 for  $\tilde{\mu}_{i(\lambda)}$  in Eq. (7), and re-arranging to solve for  $x_{i(\lambda)}$  gives:

$$x_{i(\lambda)} = \exp \left( -\tilde{\mu}_{i(\lambda)}^{\circ} + \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) \quad (8)$$

For the case of a non-ideal solution phase, an excess Gibbs energy of mixing term is added, which is a model-specific function that involves mole fractions of the species within that phase,  $x_{i(\lambda)}$  [20]. Similar to Eq. (8), the mole fraction of a species in a non-ideal phase is represented in PGE as a function of the system component potentials as follows:

$$x_{i(\lambda)} = \exp \left( -\tilde{\mu}_{i(\lambda)}^{\circ} - \tilde{\mu}_{i(\lambda)}^{\text{ex}} + \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) \quad (9)$$

Technically, the equation for  $x_{i(\lambda)}$  in Eq. (9) is *not a function* because  $\tilde{\mu}_{i(\lambda)}^{\text{ex}}$  is itself a function of  $x_{j(\lambda)}$ ,  $\forall j$ . Therefore, one can only define an

<sup>1</sup> Note that a system component may be a chemical element, an integer combination of chemical elements, or an electron corresponding to an ionic phase.

<sup>2</sup> Note that  $\Xi$  is the conjugate variable to the increase in  $C$  corresponding to ionic phases.

<sup>3</sup> Dividing by  $RT$ , where  $R$  is the ideal constant and  $T$  the absolute temperature, reduces computational expense and is standard practice.

explicit function for  $x_{i(\lambda)}$  in PGE when solution phase  $\lambda$  is ideal; however, this cannot be done when  $\lambda$  is non-ideal. For any non-ideal solution phase  $\lambda$ , replacing the expressions of chemical potentials in Eq. (9), one gets an implicit expression of the form  $x_{i(\lambda)} = f(\mu(x))$ . In PGE, the preceding expression is used to construct the mass balance residuals, which must be near zero (within tolerance) when the conditions of equilibrium are satisfied [7]. The roots, including  $x_{i(\lambda)}$ , of the non-linear system of equations so formed must then be solved, which significantly impacts the performance and stability of PGE. At this stage, one faces a difficult choice of options due to several reasons.

Firstly, since the residual equations are not explicit, solving the system of equations in order to find the mole fractions of the species requires solving an additional non-linear problem within PGE. One is faced with the question of how to evaluate the roots of an implicit expression in a closed-form sense. In Thermochemica, multiple approaches were explored to find the roots. One of these approaches was to solve for the mole fractions,  $x_{i(\lambda)}$ , at each step while computing the partial molar excess terms using the mole fractions from the previous global iteration. Though the use of this approach temporarily makes the residual equation explicit, it does not guarantee convergence especially in highly non-linear phases. Another approach was to use a linear averaged approximation of the mole fraction ( $x^{m+1} = 0.5(x^m + x^{\text{temp}})$ ) or a non-linear averaged approximation ( $x^{m+1} = \sqrt{x^m x^{\text{temp}}}$ ) but without any assurance of convergence. A more involved attempt used a nested non-linear root finding algorithm but it was often unfruitful despite adding significantly to the computational expense.

Secondly, and more critically, there might be cases where the residual equations result in a system with no roots. Such a situation cannot be dealt with using any algorithm and causes the PGE method to fail. Finally, the last issue relates to existence of multiple roots. Such a scenario can arise, for example, in systems with miscibility gaps and the roots calculated using the PGE algorithm are virtually indistinguishable and can therefore result in misleading predictions of equilibrium conditions. These predicaments are further amplified as one moves to more complicated non-linear models and higher order systems. In general, such models act as significant impediments to the applicability of PGE for determining phase equilibrium in systems where highly non-linear non-ideal phases are involved.

GEM, on the other hand, does not require a set of explicit functions of the mole fractions of the species  $x_{i(\lambda)}$ . Since the Gibbs energy and mass balance residual are simultaneously minimised in GEM, it instead requires an explicit function of chemical potentials as a function of  $x_{i(\lambda)}$ . Even without any rearrangement, the chemical potentials of species are explicit functions of mole fractions ( $\bar{\mu}_{i(\lambda)} = f(x)$ ). As a result, the roots of the resulting system of linearised equations<sup>4</sup> can be directly evaluated. Therefore, GEM does not suffer from the shortcomings of PGE and is directly applicable to all sorts of mixing models. While applying GEM, one does not need to focus on sidestepping the numerous hurdles faced by PGE when dealing with highly non-linear phases and despite the numerical disadvantages discussed by Piro et al. [7], it is much more robust and with the aid of a good initial estimate and proper line search methods it converges easily for a much broader range of models compared to PGE.

### 3. Summary

In summary, the PGE method has been found to offer marginal benefits to GEM in handling systems containing stoichiometric and ideal solution phases. However, PGE experiences a great predicament when

involving non-ideal solution phases whereby one can no longer define mole fractions as explicit functions of chemical potentials because excess Gibbs energy expressions are also functions of mole fractions. In contrast, the GEM method avoids this shortfall as it reverses the selection of dependent and independent variables, whereby the chemical potentials of solution species can be written as explicit functions of the mole fraction of solution species. In practice, the GEM method has proven to be quite robust in a number of complex thermodynamic systems involving highly non-linear excess Gibbs energy models.

### 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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<sup>4</sup> The linearised system follows from the method of Lagrange multipliers used to solve the constrained optimisation problem and derivation of such a system of equations has been presented by, for example, White et al. [9], Eriksson and Rosen [18], etc.