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Letter to the Editor

On the interpretation of chemical potentials computed from equilibrium thermodynamic codes

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Great progress has been made within the nuclear community in developing and applying thermodynamic models to better understand a variety of materials, as evidenced by the large number of publications on this subject in the Journal of Nuclear Materials. However, the interpretation of chemical potential values from equilibrium thermodynamic calculations, although numerically correct, may potentially be misleading under certain conditions. This is an important point to clarify as equilibrium thermodynamic calculations are increasingly used to augment models of various phenomena in multi-physics simulations [1].

The motivation for preparing this letter to the Editors of the Journal of Nuclear Materials is to formally address this matter as it relates to articles in this journal. Although the matters discussed herein are well understood by specialists in classical equilibrium thermodynamics, they may not be clear to a non-specialist. This letter does not imply any incorrect numerical calculation of any particular software nor does it imply any incorrect approach in performing experimental measurements; it is intended to clarify the interpretation of computed thermodynamic values to avoid any unintentional errors.

The first topic of this letter addresses the interpretation of a particular scenario that is often encountered in thermodynamic calculations whereby a binary system is predicted to be homogenous and represented by a pure stoichiometric phase that does not represent a pure element. The chemical potentials of the pure component elements may be computed internally and various thermodynamic properties may be reported, such as the thermochemical activity of other species and phases. For this scenario, we demonstrate that the thermodynamic properties derived from the chemical potentials of the component elements are not unique and the results may be misleading. As an example, the computed oxygen chemical potential in a particular model of the uranium–oxygen system may not be unique for a particular temperature and composition, and only one value of a range of possible values may be calculated. This interpretation is important when thermodynamic models guide experimental activities, such as controlling the oxygen environment in various measurements involving $UO_{2\pm x}$.

The second topic addresses the frequent inaccurate use of the term "chemical potential," which is often represented either colloquially or in formal literature as a derived thermodynamic property. This term is often expressed as the partial molar Gibbs energy of ideal mixing, which is related to the configurational entropy, while the standard reference Gibbs energy is neglected from the equation. As a point of clarity, the term 'molar' is used in this work to mean per mole, not in the sense of molarity. Although in many practical situations there are no consequences to this misrepresentation, it is nevertheless important to employ the exact expressions when relating thermodynamic calculations to other properties within multi-component systems or when coupling them to models of other physical phenomena.

Apart from maintaining precise semantics, one should be aware of two particular areas where computed chemical potentials must be precisely defined and understood. First, incorrectly relating the chemical potential of a particular species in one phase to the chemical potential of the same species in another phase, which must be identical at equilibrium, can result in unintentional errors when deriving related thermodynamic quantities. Second, the computed chemical potential – just like many other thermodynamic potentials (i.e., temperature, pressure, or electrochemical potentials) – provides the driving forces of various transport phenomena, such as solid-state diffusion or phase evolution. Therefore, incorrectly computing the chemical potential in a thermodynamic equilibrium calculation as input to a mass transport simulation could also unintentionally create errors. Both of these issues become more important when handling large multi-component systems, such as irradiated nuclear fuel.

1. Chemical potentials computed in a homogenous system with a pure stoichiometric phase

One should exercise caution when interpreting the predicted chemical potentials of the pure elements from an equilibrium thermodynamic calculation when only one stoichiometric phase is predicted to be stable. Similarly, thermodynamic quantities that may be derived from the chemical potentials, such as the thermodynamic factor or specific enthalpy, should be treated carefully. The only exception to this statement is the chemical potential of that

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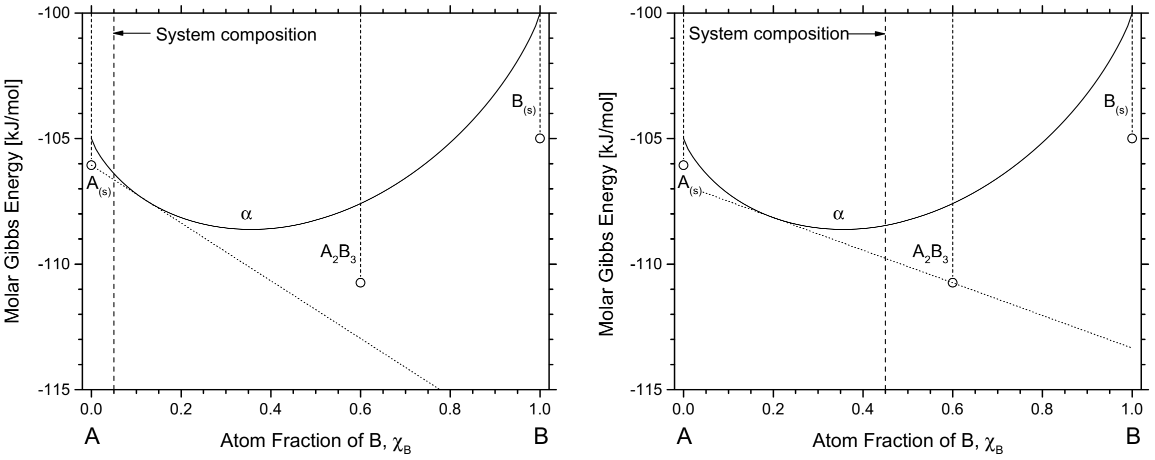
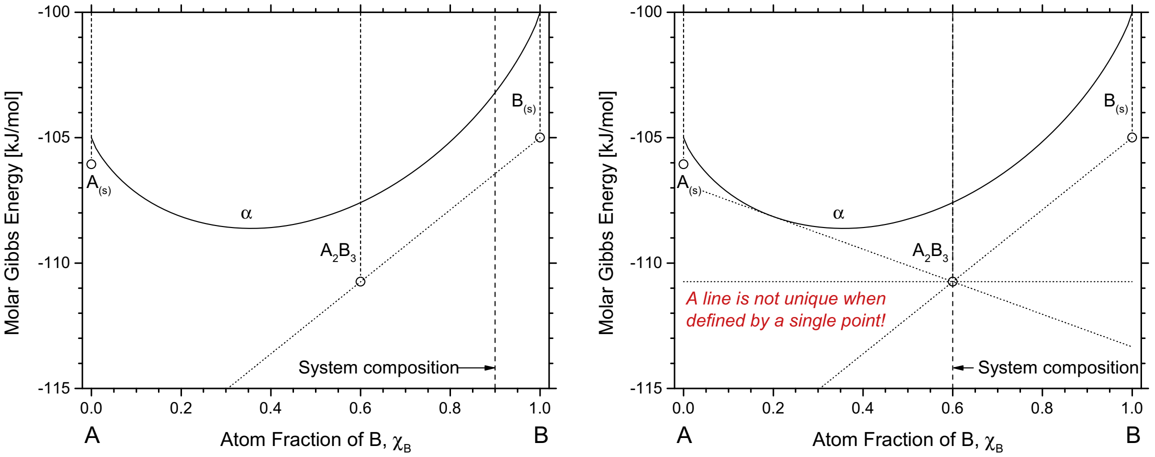


(a) $A_{(s)}$ is in equilibrium with $\alpha_{(s)}$.

(b) $A_2B_{3(s)}$ is in equilibrium with α.



(c) $A_2B_{3(s)}$ is in equilibrium with $B_{(s)}$.

(d) Only $A_2B_{3(s)}$ is stable.

Fig. 1. Four molar Gibbs energy plots (at constant temperature and pressure) are provided for an arbitrary binary system A–B consisting of three stoichiometric phases (i.e., $A_{(s)}$, $A_2B_{3(s)}$ and $B_{(s)}$) and a solid solution phase ($\alpha_{(s)}$). Tangent lines (dotted) are drawn through co-existing phases for various compositions of the system, which are represented by vertical dashed lines.

particular component and the (post-calculated) thermochemical activity of the same component in another phase. This condition does not always apply when a stoichiometric phase is predicted to be in equilibrium with another phase or if a system is predicted to be homogenous with a solution phase. This condition equally applies to higher order systems; however, a binary system is discussed herein for sake of simplicity.

Recall the definition of the chemical potential as [2]

$$\mu_i = \left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_{j\neq i}} \qquad (1)$$

where μ_i and n_i are the chemical potential and quantity of species *i*, respectively, *G* is the integral Gibbs energy of the system, *T* is the absolute temperature and finally *P* is the hydrostatic pressure of the system. The criteria for thermodynamic equilibrium established by J.W. Gibbs requires that $dG_{sys} = 0$ for a closed isothermal–isobaric system. An important equivalent statement relates the chemical potential of any species or phase within a system at thermodynamic equilibrium to the chemical potentials of the system components[1] Γ_j and the stoichiometric coefficients $\nu_{i,j}$ via the following formalism [3,4]

$$\mu_i = \sum \nu_{i,j}\Gamma_j \qquad (2)$$

An important consequence of the above equation is that the chemical potential of any species in a system at thermodynamic equilibrium is the same irrespective of the phase [3]. Furthermore, the utilization of Eq. (2) provides the foundation for a common and convenient graphical interpretation to phase equilibria in a binary system by plotting tangent lines with respect to stable phases in a molar Gibbs energy plot [5]. The lowest common tangent between phases that abides conservation of mass yields the minimum Gibbs energy of the system. In a binary closed system at constant temperature and pressure, the Gibbs Phase Rule dictates that a maximum of two phases may coexist.

Fig. 1 illustrates four molar Gibbs energy plots for an arbitrary binary system A–B consisting of three stoichiometric phases (i.e., A, A_2B_3 and B) and a solid solution phase (i.e., α). The solid curve represents the molar Gibbs energy of the solution phase and the vertical lines with an open circle represent the molar Gibbs energies of the pure stoichiometric phases. The vertical dashed line on each figure corresponds to the overall composition of each system represented by the atom fraction of component B, χ_B, which differs for each plot. The non-vertical dotted lines are tangent to

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[1] The system components represent an assemblage of the most basic independent chemical species that can capture all phases in the system. A system component is often equivalent to a chemical element; however, it may be represented by a fixed combination of chemical elements.