On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts

In an earlier Letter to the Editor of the Journal of Nuclear Materials (JNM) [1], situations were explored whereby the chemical potentials computed by an equilibrium thermodynamics code could potentially be misleading. The intent of that letter was to acknowledge specific situations that may unintentionally lead to the misinterpretation of results that may be well understood by a specialist, but may perhaps be less obvious to a non-specialist. A closely related situation may also arise from the results produced by thermodynamic calculations involving the Modified Quasi-chemical Model (MQM), which is a sophisticated model often used to represent molten salts. With the increasing interest in Molten Salt Reactor (MSR) research [2], particularly with thermodynamic modelling and related multi-physics simulations, it seems prudent to have a follow-up discussion regarding the interpretation of chemical potentials computed by equilibrium thermodynamic codes in the context of molten salts. This Letter to the Editor of JNM is intended to better inform the user of such thermodynamic software using models specific to molten salts who may be a non-specialist. Furthermore, these matters may be of important interest when integrating thermodynamic calculations in multi-physics codes to prevent numerical instabilities.

In one particular scenario explored by Piro et al. [1], the fictive A-B system was considered with 2 mol of A and 3 mol of B. For this specific situation, only the A_2B_3 phase is stable at equilibrium. As shown in Fig. 1, the system is homogeneous and the lowest common tangent line (representing the equilibrium state, also called the "Gibbs Plane" [3]) is tangent to this phase; however, the line is not uniquely defined. This is shown graphically in Fig. 1, whereby a line cannot be uniquely defined by a single point. The tangent line could conceivably be drawn between A_2B_3 and either $B_{(s)}$ or α (with zero moles); however, there is no basis for selecting zero moles of one phase or the other.

For this particular scenario, the system is under-determined when the system components[1] are taken as A and B. One may be under the false impression that the chemical potentials of A and B have been determined, whereas these are in fact undefined due to the misidentification of the system components — for this particular situation, the system components A and B should be re-defined to a single system component: A_2B_3. As the International Union of Pure and Applied Chemistry defines the term 'component': "The number of components in a given system is the minimum number of independent species necessary to define the composition in all the phases of a system" [4]. Since the minimum number of species required to define this is one (i.e., A_2B_3), the system components should be re-defined from A and B to A_2B_3 for this particular scenario.

Due to the mathematical nature of the MQM model, one can easily misinterpret calculated chemical potentials of some components for similar reasons. The MQM class of models, which has been advanced primarily by Pelton et al. [5–8], has been used with great success to model various fluoride [9–12] and chloride salts [9,13] for nuclear applications. This model is currently implemented in FACTSAGE [14] and THERMOCHIMICA [15]. The fundamental premise of this model is to shift focus from the interaction of species to the interaction of pairs of species (or quadruplets) in an effort to capture short range ordering. For example, if one has a solution model comprised of species C and D, then one would be concerned with interactions of C—C, D-D, and C-D pairs. Equilibrium calculations are centred on the chemical potentials of the pairs (or quadruplets) rather than the species.[2] Furthermore, the model involves two sublattices, which do not include vacancies; therefore, every phase component (or 'compound end member') is necessarily a compound and not a pure element. The importance of this feature of the model is that the representation of the phase in composition space is limited by the compounds — not the elements — and will be further explained in the following paragraphs.

One can model a familiar material of interest to the MSR community, LiF—BeF$_2$ (aka. "FLiBe"), with MQM. The model produced by Beneš and Konings [16] assigns the species as LiF and BeF$_2$, which produces the following pairs: LiF—LiF, BeF$_2$—BeF$_2$, and LiF—BeF$_2$. A thermodynamic database of the Li—Be—F system may include other phases in addition to this molten salt, such as various stoichiometric solid phases and an ideal gas mixture. Some of these non-salt species may not necessarily correspond to LiF or BeF$_2$,

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[1] The terms 'phase component' and 'system component' are used here to differentiate a component of a phase (synonymous with 'species' or 'compound end member') from a component of a system, which may be a pure element, a compound, or electron (corresponding to an ionic phase).

[2] Note that internal to a Gibbs energy minimizer, the number of moles of the pairs are used as independent variables rather than those of the species. This is an important point to enable effective execution of equilibrium calculations, as explained by Pelton et al. [5].
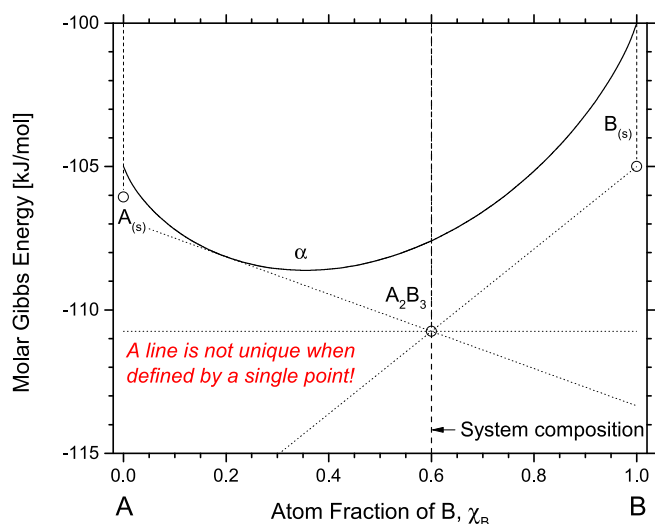
Fig. 1. The fictive A-B system is shown with the overall composition identified, which intersects the A_2B_3 phase. The lowest common tangent line intersects this phase, but is not uniquely defined. Copied from Piro et al. [1].

which may include the pure elements (e.g., $F_{2(g)}$).

Suppose one were to define the system components by the chemical elements (i.e., Li, Be, and F) while assigning mass quantities to the system that precisely correspond to LiF and BeF_2, and a specified temperature and pressure that together yield a homogeneous system with only a molten salt being stable. This would be a typical calculation using an equilibrium solver. The composition space of this system is illustrated in Fig. 2. In this situation, there are three phase components (i.e., $LiF-LiF$, BeF_2-BeF_2, and $LiF-BeF_2$) and three system components (i.e., Li, Be, and F); however, one cannot uniquely define the Gibbs Plane because the three points are co-linear in three dimensional space. In more mathematical terms, the Hessian matrix is rank deficient.
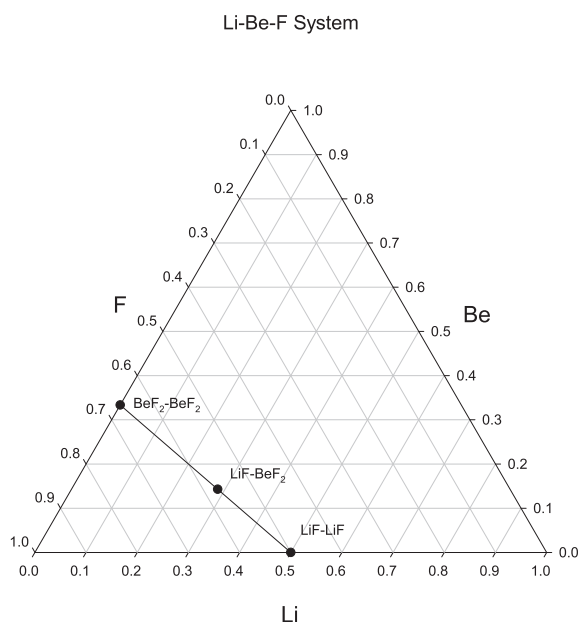

Fig. 2. A ternary plot of the $Li-Be-F$ system with the three pair fractions corresponding to $LiF-BeF_2$ are indicated. A three dimensional Gibbs plane cannot be defined by three points because they are colinear.

Since the Gibbs Plane is used to define all chemical potentials in the system and it is not uniquely defined for this scenario, not all chemical potentials in the system are uniquely defined. The only uniquely defined chemical potentials in this system lie on the $LiF-BeF_2$ line and anything outside from that is not unique. Of particular interest to the MSR community, the fluorine potential — and the corresponding thermochemical activity of fluorine — is not uniquely defined for this situation. This scenario is analogous to the one shown in Fig. 1, whereby one could potentially compute a fluorine potential, but it would not be uniquely defined. The issue here is that the user may receive from the software a numerical value of the chemical potential or thermochemical activity of fluorine that is meaningless and misleading. A more mathematically rigorous proof is provided in the Appendix, which shows that the Hessian matrix used in Gibbs energy minimization is underdetermined for this situation. It may be possible to still computationally solve the Hessian, but that would only be possible due to very minor machine imprecisions.

Note that one would have a uniquely defined system for this situation if the system components were instead defined as LiF and BeF_2. Alternatively, one could also have a uniquely defined system if there was a slight surplus or deficit of one of the chemical elements, which would effectively shift the system off the line shown in Fig. 2. In that situation, conservation of mass would require another phase to be stable in addition to the salt. Graphically, one could interpret that situation as a three-dimensional Gibbs plane defined by three points that are co-linear (corresponding to the salt, akin to Fig. 2) in addition to some additional point(s) (representing a secondary phase).

To summarize, the MQM model has been effectively used to capture the thermodynamic behaviour of various salts for MSR applications. To avoid potentially misinterpreting calculated chemical potentials and other thermodynamic quantities, which may be non-unique, recommendations are made to the user to be conscientious of the appropriateness of selecting the system components. If the overall system composition can be defined by a reduced set of compounds that do not correspond directly to the chemical elements, then the user should define them as such. While these matters may be familiar and clear to a thermodynamics specialist, the intent of this letter is to assist non-specialists in interpreting and executing such calculations, particularly those involved with MSR research.

Acknowledgements

Appendix

Mathematically, Gibbs energy minimization is a constrained non-convex optimization problem with the objective of determining a unique combination of system potentials that yields a minimum in Gibbs energy of the system while satisfying mass balance constraints and the Gibbs phase rule under isothermal isobaric conditions. The objective is often achieved using the method of Lagrange multipliers that simultaneously minimizes the integral Gibbs energy and the residuals of mass balance equations. This results in a system of linearized equations that can be written in matrix form as [17]:

$$\mathbf{H} \cdot \boldsymbol{\pi} = \boldsymbol{\zeta} \tag{1}$$

where $\boldsymbol{\pi}$ and $\boldsymbol{\zeta}$ denote the unknown and constraint vectors respectively, and the Hessian matrix ($\mathbf{H}$) can be written as [17,18]:

$$
\mathbf{H} = \begin{bmatrix}
r_{j=1,k=1} & \cdots & r_{j=1,k=C} & \phi_{j=1,\lambda=1} & \cdots & \phi_{j=1,\lambda=\Lambda} & \nu_{j=1,\omega=1} & \cdots & \nu_{j=1,\omega=\Omega} \\
\vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
r_{j=C,k=1} & \cdots & r_{j=C,k=C} & \phi_{j=C,\lambda=1} & \cdots & \phi_{j=C,\lambda=\Lambda} & \nu_{j=C,\omega=1} & \cdots & \nu_{j=C,\omega=\Omega} \\
\phi_{\lambda=1,j=1} & \cdots & \phi_{\lambda=1,j=C} & 0 & \cdots & 0 & 0 & \cdots & 0 \\
\vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
\phi_{\lambda=\Lambda,j=1} & \cdots & \phi_{\lambda=\Lambda,j=C} & 0 & \cdots & 0 & 0 & \cdots & 0 \\
\nu_{\omega=1,j=1} & \cdots & \nu_{\omega=1,j=C} & 0 & \cdots & 0 & 0 & \cdots & 0 \\
\vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
\nu_{\omega=\Omega,j=1} & \cdots & \nu_{\omega=\Omega,j=C} & 0 & \cdots & 0 & 0 & \cdots & 0
\end{bmatrix}
\tag{2}
$$

where C is the number of system components, λ is an index of a solution phase, of which there are Λ in the system, ω is an index of a stoichiometric phase, of which there are Ω in the system, $\nu_{i,j}$ is the stoichiometric coefficient of component j in species i, and $r_{j,k}$ and $\phi_{j,\lambda}$ can be expressed as follows:

$$
r_{j,k} = \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_\lambda} n_{i(\lambda)} \nu_{i,j} \nu_{i,k},
\tag{3}
$$

$$
\phi_{j,\lambda} = \sum_{i=1}^{N_\lambda} n_{i(\lambda)} \nu_{i,j}.
\tag{4}
$$

N_λ is the number of species in phase λ, and $n_{i(\lambda)}$ is the number of moles of species i in solution phase λ. Clearly, $r_{j,k} = r_{k,j}$ and $\phi_{j,\lambda} = \phi_{\lambda,j}$, which yields a symmetric matrix for $\mathbf{H}$.

The example of the FLiBe system discussed above is used to illustrate the under-determined nature of the Hessian matrix with improperly chosen system components. Consider a homogeneous system in which the only phase present is a solution phase represented by the MQM model. Suppose the system composition falls somewhere along the $BeF_2 - LiF$ composition line illustrated in Fig. 2, and thus the phase components are LiF−LiF, BeF_2−BeF_2, and LiF−BeF_2, and the system components are Li, Be, and F. For this case $C = 3$, $\Lambda = 1$, $N_1 = 3$, and $\Omega = 0$. This results in a 4×4 Hessian matrix as follows:

$$
\mathbf{H} = \begin{bmatrix}
r_{1,1} & r_{1,2} & r_{1,3} & \phi_{1,1} \\
r_{1,2} & r_{2,2} & r_{2,3} & \phi_{2,1} \\
r_{1,3} & r_{2,3} & r_{3,3} & \phi_{3,1} \\
\phi_{1,1} & \phi_{2,1} & \phi_{3,1} & 0
\end{bmatrix}.
\tag{5}
$$

The stoichiometry matrix ν is:

$$
\nu = \begin{bmatrix}
2 & 0 & 2 \\
0 & 2 & 4 \\
1 & 1 & 3
\end{bmatrix}.
\tag{6}
$$

where the rows represent LiF−LiF, BeF_2−BeF_2, and LiF−BeF_2, and the columns represent Li, Be, and F. Taking the current estimate of the number of moles of each species to be the arbitrary values n_1, n_2, and n_3, $\mathbf{H}$ is then:

$$
\mathbf{H} = \begin{bmatrix}
4n_1 + n_3 & n_3 & 4n_1 + 3n_3 & 2n_1 + n_3 \\
n_3 & 4n_2 + n_3 & 8n_2 + 3n_3 & 2n_2 + n_3 \\
4n_1 + 3n_3 & 8n_2 + 3n_3 & 4n_1 + 16n_2 + 9n_3 & 2n_1 + 4n_2 + 3n_3 \\
2n_1 + n_3 & 2n_2 + n_3 & 2n_1 + 4n_2 + 3n_3 & 0
\end{bmatrix}.
\tag{7}
$$

This Hessian is rank-deficient, with the first three columns linearly dependent, and thus has a determinant of 0. Therefore, any attempt to solve the corresponding system of linear equations will fail. Note that in practice it is possible that the system of equations can be solved with a sufficient numerical error associated with machine precision, which will yield some mathematically meaningless results. In this case, one must rely heavily on the quality and robustness of the linear equation solver employed.

If one were to instead take the system components as LiF and BeF_2, C is reduced to 2, and the Hessian is of the 3×3 form:

$$
\mathbf{H} = \begin{bmatrix}
r_{1,1} & r_{1,2} & \phi_{1,1} \\
r_{1,2} & r_{2,2} & \phi_{2,1} \\
\phi_{1,1} & \phi_{2,1} & 0
\end{bmatrix}.
\tag{8}
$$

In this case, the stoichiometry matrix is:

$$
\nu = \begin{bmatrix}
2 & 0 \\
0 & 2 \\
1 & 1
\end{bmatrix}.
\tag{9}
$$

where the rows represent LiF−LiF, BeF_2−BeF_2, and LiF−BeF_2, and the columns LiF and BeF_2. The Hessian is then:

$$
\mathbf{H} = \begin{bmatrix}
4n_1 + n_3 & n_3 & 2n_1 + n_3 \\
n_3 & 4n_2 + n_3 & 2n_2 + n_3 \\
2n_1 + n_3 & 2n_2 + n_3 & 0
\end{bmatrix}.
\tag{10}
$$

This matrix is non-singular, and its determinant is:

$$
\text{Det}(\mathbf{H}) = -4(n_1 + n_2 + n_3)(4n_1 n_2 + n_1 n_3 + n_2 n_3).
\tag{11}
$$

This determinant is always non-zero, as the values n_1, n_2, and n_3 must all be greater than zero and real. This example illustrates how an under-determined system of equations representing a phase represented in MQM form can be converted to a full-rank system by reducing the number of system components to a more appropriate form.

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