Combining reaction kinetics to the multi-phase Gibbs energy calculation

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Abstract

Development of robust and efficient methods for the computation of multi-phase systems has long been a challenge in both chemical and petroleum engineering as well as in materials science. Several techniques have been developed, particularly those which apply the Gibbs free energy minimization. In addition to calculation of global equilibrium problems, practical process simulation would benefit from algorithms, where reaction rates could be taken into account. In the present work, the method of Lagrange multipliers has been used to incorporate such additional constraints to the minimization problem, which allow a mechanistic reaction rate model to be included in the Gibbsian multi-component calculation.

The method can be used to calculate the thermodynamic properties of a multi-phase system during a chemical change. The applications include computational materials science, industrial process modeling with known reaction rates combined with complex heat and mass transfer effects and studies of other non-equilibrium systems.

Keywords

Gibbs energy minimization, reaction rate constraint, modeling of multi-phase processes

1. Introduction

Several industrial processes in the fields of chemistry, petroleum engineering, metallurgy, steel-making or e.g. in pulp and paper manufacturing include production stages, where chemical changes occur in true multi-phase fashion. The quantitative treatment of such processes is best performed with thermodynamic multi-phase methods. In a complex reactive system, where several phases can form, the minimum of Gibbs energy provides a general criterion for equilibrium calculations. Yet, many of the problems involve non-equilibrium reactions and processes, for which the Gibbs'ian approach as such is not applicable. Consequently, there has been a search for ways to link reaction kinetics and multi-component thermodynamic calculations.

While performing the Gibbs energy minimization the calculation is usually constrained by the mass balance of the closed system. As a result, the global equilibrium composition at a given temperature and pressure is reached. In what follows, a Gibbs free energy technique based on the extension of the (stoichiometric) conservation matrix of the Lagrange method is presented. The extension of the conservation matrix can be used to include reaction kinetic restrictions to control the extent of selected chemical reactions in terms of their reaction rates.

2. Setting rate constraints into the Gibbs energy calculation

2.1. Gibbs free energy minimization by the Lagrange method

The Gibbs free energy of the multicomponent system is written in terms of the chemical potentials as follows

$$G = \sum_{\alpha} \sum_{k} n_k^{\alpha} \mu_k^{\alpha} \qquad (1)$$

where μ_k^{α} is the chemical potential of the species (k) in the respective phase α and n_k^{α} is its molar amount. The respective chemical multi-component system with N constituents, which are formed of l components can be described with a ($N \times l$) conservation matrix **A**, the element of which is a_{kj}, defining the stoichiometry of component j in the respective constituent k.

The minimization of the Gibbs free energy can be performed by using several alternative techniques [1-2]. Perhaps the most widespread mathematical routine is that of Lagrangian multipliers, where a new function (L) is defined in terms of the mass balance relations of the system components:

$$L = G - \sum_{j}^{l} \lambda_j \phi_j \qquad (2)$$

where λ_j's are the undetermined multipliers of the Lagrange method and ϕ_j represent the mass balances of the system components. Using these and the partial derivatives of the Lagrange function, the Gibbs energy minimum can be solved in terms of the equilibrium molar amounts at a given temperature and pressure. The Lagrange multipliers as well become solved representing the equilibrium chemical potentials of the system components [1,3,4]. Thus, for the chemical potentials of any constituent k there is:

$$\mu_k = \sum_{j=1}^{l} a_{kj} \lambda_j \quad (k = 1,2,...N) \qquad (3)$$

Equation (3) gives the chemical potential of any constituent k as a linear combination of the respective potentials of the system components.

The multi-phase system may also be reaction rate controlled or influenced by other stress- or field- related factors, in which case additional constraining equations are needed. It is often possible to find such extension of the conservation matrix by which a new Lagrangian multiplier can be used to solve the constraint potential in the multi-phase system [3].

The conservation matrix $\mathbf{A}'$ of the additionally constrained system is made up of the coefficients of all conservation equations valid in the system. The rows of the matrix represent again its altogether N constituents. When merely chemical reaction equilibria are considered, the conventional stoichiometric relations determine the conservation of atoms of elements and electric charge and there are l respective columns for these. When additional conservation equations are required, the new constraint appears as an additional column ($l+1$) in the conservation matrix:

$$\mathbf{A}' = \begin{pmatrix} a_{1,1} & \cdots & a_{1,l} & a_{1,l+1} \\ \vdots & \ddots & \vdots & \vdots \\ a_{N_1,1}^{(1)} & \cdots & a_{N_1,l}^{(1)} & a_{N_1,l+1}^{(1)} \\ a_{N_1+1,1}^{(2)} & \cdots & a_{N_1+1,l}^{(2)} & a_{N_1+1,l+1}^{(2)} \\ \vdots & \ddots & \vdots & \vdots \\ a_{N,1}^{(\Psi)} & \cdots & a_{N,l}^{(\Psi)} & a_{N,l+1}^{(\Psi)} \end{pmatrix} \qquad (4)$$

Here the matrix elements for the stoichiometric phase constituents are presented in the firs l columns and the additional column ($l+1$) represents the new conservation equation. Thus, the matrix element $a_{k,l+1}^{\alpha} = 0$ for all those

constituents k, which are not affected by the additional constraint, whereas $a^{\alpha}_{k,l+1}$ is *not zero* for those constituents, which are affected by the said constraint. The mass balance of the total system is not affected, if the molecular mass of the component M_{l+1} is chosen to be zero.

When using $\mathbf{A'}$, the solution of $\min(G)$ again results with equation (3), that is the chemical potentials of the constituents become solved in terms of the elements of the extended matrix and the respective Lagrange multipliers. There will be one new multiplier for each new constraint equation, and they then represent either physical factors such as the electrochemical part of a chemical potential or constrained affinities [3].

2.2. Systems with kinetically constrained reactions

The above method can be used to conserve the amount of a species at its input value in a Gibbs'ian calculation. This value can then be algorithmically connected to a reaction rate, and a series of Gibbs energy calculations be performed where one or several species only change with a given reaction rate.

If several conditions for kinetically constrained species are used, the (non-zero) affinities of the chemical reactions are derived by using equation (3) and the stoichiometric coefficients of reactants and products in the constrained system [5]. The result can be summarized in the following two equations:

$$\sum_k v_k \, \mu_k = \sum_k v_k \sum_{j=1}^{l} a_{kj}\lambda_j = 0 \quad \text{(equilibrium reactions)} \tag{5}$$

$$\sum_k v_k \, \mu_k = \sum_k v_k \sum_{j=l+1}^{l'} a_{kj}\lambda_j \neq 0 \quad \text{(kinetically constrained reactions)} \tag{6}$$

where v_k is the stoichiometric coefficient (positive for a product, negative for a reactant) for the species k in the reaction in question; l' is the number components in the system including those defined for kinetic restrictions.

2.3. Calculation of the rutilisation system with the Gibbsian method

To avail the use of the method in a wide-spread thermochemical platform which utilizes the Lagrange multiplier technique, a further practical trick has been used. When e.g the program ChemApp [6] is applied as the free energy minimiser, the conservation matrix is usually given with constant (stoichiometric) coefficients. To enable constraining of forward and reverse reactions, the matrix is further extended by introducing a new row to control the desired reactions. For a single reaction, the rows can be denoted with R+ and R-, as they are connected to the constraint component R with non-zero a_{kj}-values.

Both of them are defined as stoichiometric phases for system input definitions, but are not allowed to present in the calculated state of Gibbs energy minimum. For the formation reaction R+, a_{kj} =1 and for the decomposing R- , a_{kj} =-1. The respective connection to the actual species, which are kinetically conserved, must also have non-zero stoichiometric matrix elements. The standard chemical potentials, which appear as input data in the calculation, are set to zero for the phases R+ and R-. More than one species can again be involved and the corresponding a_{kj}-values become defined by the actual reaction stoichiometry.

Table 1. Data for the TiO(OH)$_2$ calcination reactions (T = 1000 C)

Reaction	ΔH kJ·mol^{-1}	ΔG kJ·mol^{-1}	Reaction rate equation	E_a kJ·mol^{-1}	A h^{-1}
TiO(OH)$_2$ ↔ TiO$_2$(An) + H$_2$O↑	43.5	-83.6	assumed equilibrium	-	-
TiO$_2$(An) → TiO$_2$(Ru) (kinetically constrained reaction)	-6.6	-5.9	$\xi = 1-(1-kt)^3$	441.99	1.8E+17

In Table 1., a simple system representing Titanium oxyhydrate [TiO(OH)$_2$] calcination is described. From experience it is known that the H$_2$O release from the oxyhydrate is a fast reaction at ca. 180 C. The anatase-rutile–transformation is a slow, yet spontaneous, solid state reaction, for which the rate constant (k) is known in terms of the activation energy (E_a) and frequency factor (A). In table 2, the conservation matrix and its extension to include one reactive component R is presented. The shaded area shows the non-restricted equilibrium system.

Table 2. Stoichiometric matrix for the kinetically constrained rutilisation system

Species	H$_2$O	TiO$_2$	R
H$_2$O-gas	1	0	0
TiO(OH)$_2$	1	1	0
TiO$_2$(An)	0	1	0
TiO$_2$(Ru)	0	1	1
R+	0	0	1
R-	0	0	-1

In Figure 1, the time-dependent rutile [TiO$_2$(Ru)] fraction $\xi=\xi(t)$ is solved by using the constrained Gibbs energy minimization method. At each constant temperature the Gibbs energy appears as a monotonically descending curve (only the curve for 950 C is shown).
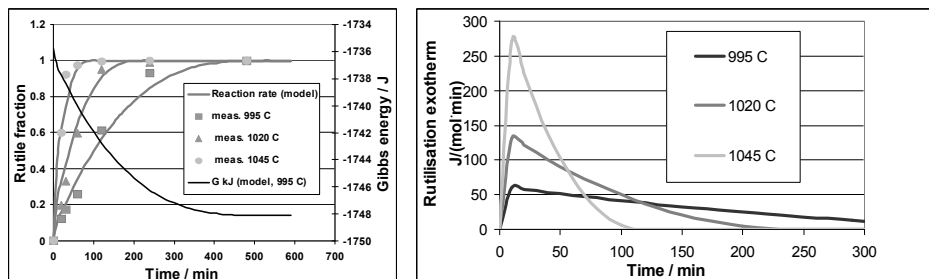
Figure 1. Use of a reaction rate constraint in a thermodynamic Gibbs energy system. The coupled model is also used to calculate the time-dependent exotherm of the rutilisation reaction. Reaction rate data is given in table 1.

3. Conclusions

The presented method can also be used to introduce more complex mechanisms into a multi-component calculation. The matrix **A** must be extended with one column and two rows for each kinetically constrained species [6]. Though the method was developed by using Lagrangian undetermined multipliers, the fundamental equations (3)-(6) derived from the extremum condition are strictly thermodynamic and do not depend on the mathematical method. Thus, a similar approach can be pursued for when applying other minimization procedures.

The combination of reaction rates with the multi-component method enables direct calculation of the thermodynamic state properties during a chemical change. The obvious advantage of such models is the simultaneous and interdependent calculation of all thermochemical changes in the process, which opens new possibilities for advanced multi-phase simulation.

Acknowledgements

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