

## A Gibbs energy minimization method for constrained and partial equilibria\*

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**Abstract:** The conventional Gibbs energy minimization methods apply elemental amounts of system components as conservation constraints in the form of a stoichiometric conservation matrix. The linear constraints designate the limitations set on the components described by the system constituents. The equilibrium chemical potentials of the constituents are obtained as a linear combination of the component-specific contributions, which are solved with the Lagrange method of undetermined multipliers. When the Gibbs energy of a multiphase system is also affected by conditions due to immaterial properties, the constraints must be adjusted by the respective entities. The constrained free energy (CFE) minimization method includes such conditions and incorporates every immaterial constraint accompanied with its conjugate potential. The respective work or affinity-related condition is introduced to the Gibbs energy calculation as an additional Lagrange multiplier. Thus, the minimization procedure can include systemic or external potential variables with their conjugate coefficients as well as non-equilibrium affinities. Their implementation extends the scope of Gibbs energy calculations to a number of new fields, including surface and interface systems, multiphase fiber suspensions with Donnan partitioning, kinetically controlled partial equilibria, and pathway analysis of reaction networks.

**Keywords:** Donnan equilibrium; extent of reaction; Gibbs energy; immaterial constraints; minimization; surface energy; virtual components.

### INTRODUCTION

The development of functional materials and innovative processes, so often asked for in contemporary society, require quantitative and interdisciplinary predictions connecting the appropriate physical, chemical, and even biological phenomena. In macroscopic systems, where thermal, electrical, and mechanical variables appear interconnected with the chemistry of the system, the thermodynamic free energy is the most general property to be applied for relationships between different quantities.

The conventional technique for multiphase systems is the minimization of the Gibbs (free) energy to solve for equilibrium compositions at constant temperature and pressure. The results are used for phase formation studies, generation of phase diagrams, and simulation of thermochemical processes occurring in complex systems. The Gibbsian approach is based on experimental thermodynamic properties and phase equilibria, the data of which is then assessed and organized by application-specific computer programs. Both new experimental techniques and evolving ab initio calculations are being used to augment the existing databases.

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The book by Smith and Missen [1] further remains the sole comprehensive treatise on numerical calculation of multicomponent chemical equilibria by Gibbs energy minimization. The development of such computer programs has continued nearly a half-century [2–4]. Additional features and improved calculation techniques have been adapted during the decades while taking advantage of the constantly improving computer capabilities. The pursuit for reliable phase diagrams has created an evolving tradition of Gibbs free energy calculations in metallurgy and high-temperature materials science [5,6]. The benefits of the multiphase free energy methods have also been increasingly utilized in chemical and petroleum engineering [7,8]. A bibliography of Gibbs energy methods in process calculations is presented, for example, by Nichita et al. [9]. Calculation of concentrated aqueous solutions is another quickly developing field with industrial interest [10,11]. Furthermore, there have been efforts in applying the Gibbsian multiphase technique to pulp suspensions, since there is a worldwide industry that manufactures pulp and paper products and operates the adjacent chemical recovery processes [12–14].

The conventional  $\min(G)$  algorithms use constrained optimization, in which the feasible solution space is determined by the (stoichiometric) conservation matrix of elemental amounts. Lampinen applied immaterial constraining for the conservation of (battery) charge when dealing with the electro-motive force of electrochemical cells [15]. Alberty [16] reported a structured method to create an extra entity constraint without connection to the material content of the system. Due to the limited reactivity of carbon atoms in benzene rings, he derived a static constraint by calculating the left null space of a reaction matrix so as to conserve the “aromaticity” of these compounds. Keck [17] used the term “generalized constraints” for describing the constraints not immediately associated with atom conservation while introducing a passive reaction rate constraint for selected reactants or products, applied in fuel combustion calculations and already used in an early publication by Keck and Gillespie [18].

The introduction of an “image component” by Koukkari [19] allowed for the use of an active reaction rate constraint within the Gibbsian calculation. A static immaterial constraint was used by Koukkari et al. [13] to model the Donnan partitioning in fiber suspensions. The method of immaterial constraints was then generalized to model, for example, surface tension, electrochemical potentials, and rate-controlled affinities in multicomponent systems [20] and called the constrained free energy (CFE) technique. Pajarre et al. [21] describe several practical applications that deal with this approach. Blomberg and Koukkari [22] reported entity conservation implementations related to transformed Gibbs energies for primarily biochemical systems. In short, the method of generalized immaterial constraints enables the association of the conservation matrix with structural, physical, chemical, and energetic attributes, extending the scope of free energy calculations beyond the conventional studies of global chemical equilibria and equilibrium-phase diagrams.

## THE MINIMIZATION PROBLEM WITH IMMATERIAL CONSTRAINTS

When additional energy or work terms affect the Gibbs free energy [ $G = G(T, P, n_k)$ ], it is customary [23] to transform the total differential of the Gibbs function to read as follows:

$$dG = S dT + V dp + \sum \mu_k dn_k + \sum z_k F \varphi_k dn_k + \sigma \sum dA_k + \dots \quad (1)$$

Here  $S$  denotes the entropy and  $V$  the volume of the system,  $\mu_k$  is the chemical potential of the species ( $k$ ),  $T$  is temperature,  $P$  is pressure, and  $n_k$  refers to mole amounts of chemical substances. The two last terms refer to additional energy effects due to electrochemical potential ( $\varphi_k$ ) and surface energy ( $\sigma$ ), with  $F$  being the Faraday constant,  $z_k$  the charge number, and  $A_k$  the molar surface area of species  $k$ . As the Gibbs energy is an additive extensive function, further terms due to either systemic or external force fields are entered, respectively [24].

Gibbs energy minimization requires optimization of the nonlinear  $G$ -function with linear constraints and can be performed by the Lagrange method of undetermined multipliers. In the conventional method, the molar amounts (mass balances) appear as necessary constraints. To incorporate the additional phenomena, a method with analogous immaterial constraints is needed. Thus, the question reverts

to one of the fundamental problems in computational thermodynamics, i.e., to convex minimization of the nonlinear objective function with its linear constraints. Gibbs energy is calculated as the sum of all molar Gibbs energies, weighted by the respective molar amounts. The sum contains all constituents as they may be chemical species in different phases, organic isomer groups, transformed biochemical metabolites, or even virtual species.

$$G = \sum_k^N n_k \mu_k \quad (2)$$

where  $n_k$  is the molar amount of constituent  $k$ ,  $\mu_k$  is the molar Gibbs energy of constituent  $k$ ,  $N$  is the number of constituents, and  $G$  is the system Gibbs energy, objective function.

The objective function of the minimization problem is nonlinear because the chemical potentials are functions of the molar amounts. The detailed mathematical expressions for the chemical potentials/molar Gibbs energies depend greatly on the applied phase models. The linear constraints denote the balance equations set on the components forming the constituents of the system. The conservation matrix is the core of the matrix equation expressing these limitations.

$$\mathbf{C}^T \mathbf{n} = \mathbf{b} \quad (3)$$

here,  $\mathbf{C}$  is the conservation matrix,  $\mathbf{n}$  is the molar amount vector for the constituents, and  $\mathbf{b}$  is the molar amount vector for the components.

Together, eqs. 2 and 3 constitute the problem for the nonlinear program (NLP) to be solved:

$$\min G(\mathbf{n}) \text{ s.t. } \quad \mathbf{C}^T \mathbf{n} = \mathbf{b} \quad ; \quad n_k \geq 0 \quad \forall k \quad (4)$$

The global minimum represents the equilibrium state with the lowest energy reachable with the given set of constraints. The constraints typically refer to elemental abundances of a closed thermodynamic system, but, as stipulated above, may include conservation of various attributes or entities [20,25]. The solution may also be referred to as a constrained equilibrium or “virtual state” (without the word equilibrium) if constraints of dynamic character have been used [18,19].

The Lagrangian objective function to be minimized then becomes as follows:

$$L = G - \sum_j^{NC} \pi_j \left[ \sum_{\alpha}^{\Omega} \sum_k^{N_{\alpha}} c_{kj} n_k^{\alpha} - b_j \right] \quad (5)$$

where  $\pi_j$  are the undetermined Lagrange multipliers used to include the constraints into the objective function  $L$ ,  $NC$  is the number of components in the system, and superscript  $\alpha$  refers to phase, while  $\Omega$  is the total number of phases [1]. The solution of the extremum problem then provides both the Lagrange multipliers and the equilibrium amounts of constituents. The summation includes all system components, whether elemental abundances or immaterial or even virtual entities. The chemical potential of each chemical species remains the linear combination of the Lagrange multipliers as defined by the elements of the conservation matrix:

$$\mu_k = \sum_{j=1}^{NC} c_{kj} \pi_j \quad (k = 1, 2, \dots, N) \quad (6)$$

The Gibbs energy in terms of the Lagrange multipliers and the total amounts of the components are, respectively

$$G = \sum_{j=1}^{NC'} b_j \pi_j + \sum_{j=NC'+1}^{NC} b_j \pi_j \quad (7)$$

Supposing that the “stoichiometric part” ( $j \leq NC'$ ) of the conservation matrix  $C$  defines entirely the amounts of elements and electrons (mass balance) of the given system, the additional components ( $NC' < j \leq NC$ ) descend from various immaterial sources affecting the free energy of the system. The physical meaning of the Lagrange multipliers is then evident as the equilibrium potentials of the components of the system. In the conventional Gibbs energy minimization method they give the chemical potentials of the elements or other stoichiometrically defined components of the equilibrium system. More generally, they represent the energy contribution of any appropriate property to the molar Gibbs energy of a constituent.

The introduction of immaterial constraints into the minimization problem then reduces to finding the appropriate form for the conservation matrix  $C$  when the work or affinity-related terms affect the chemical composition of the system. In general,  $C$  is of the following form:

$$C = \begin{pmatrix} c_{1,1}^{(1)} & \cdots & c_{1,NC'}^{(1)} & \cdots & c_{1,NC}^{(1)} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ c_{N_1,1}^{(1)} & \cdots & c_{N_1,NC'}^{(1)} & \cdots & c_{N_1,NC}^{(1)} \\ c_{N_1+1,1}^{(2)} & \cdots & c_{N_1+1,NC'}^{(2)} & \cdots & c_{N_1+1,NC}^{(2)} \\ \vdots & \cdots & \vdots & \ddots & \vdots \\ c_{N,1}^{(\Omega)} & \cdots & c_{N,NC'}^{(\Omega)} & \cdots & c_{N,NC}^{(\Omega)} \end{pmatrix} \quad (8)$$

In the conventional method, the components represent elemental building blocks of the constituents and the matrix elements  $c_{kj}$  are the respective stoichiometric coefficients. For example, the chemical potential of carbon dioxide ( $\text{CO}_2$ ) in an equilibrium system with the elements carbon (C) and oxygen (O) as system components will be given in terms of their potentials.  $\text{CO}_2$  consists of one unit of carbon and two units of oxygen, and the equilibrium chemical potential is accordingly  $\mu_{\text{CO}_2} = \pi_{\text{C}} + 2 \pi_{\text{O}}$ . In eq. 8, the matrix elements for the material-phase constituents remain equivalent with the conventional approach, but the additional column with subscript  $NC' + 1$  represents a new conservation equation. Thus, the element  $c_{k,NC'+1} = 0$  for all those constituents  $k$  which are not affected by the additional constraint, whereas it is not zero for those constituents which are affected by the said constraint. The mass balance of the total system remains unaltered if the molecular mass of the additional component,  $M_{m+1}$ , is chosen to be zero. Thus, by using immaterial components, additional conservation conditions can be included into the minimization of the objective function. In Table 1, characteristic examples of the immaterial constraints with their conjugate potentials applicable in  $\min(G)$  problems have been collected. In what follows, some characteristic examples of thermodynamically meaningful systems with immaterial components will be presented.

**Table 1** Immaterial constraints and their conjugate potentials used in CFE models.

System	Constraint	Conjugate potential	Practical examples
Chemical equilibrium systems	$\sum_{k=1}^N c_{kj} n_k = b_j$	$\pi_j = \frac{\partial G}{\partial b_j}$	Multiphase chemical equilibria Phase diagrams
Systems with area constraints	$\sum_{k=1}^{N_s} \frac{A_k n_k^s}{A_0} = \frac{A}{A_0}$	$\pi_{\text{area}} = \frac{\partial G}{\partial b_{(\text{area})}} = \sigma A_0$	Surface and interfacial tension, sorption phenomena, surface compositions
Systems with volume constraints	$\sum_{k=1}^{N_s} \frac{V_k n_k^\alpha}{V_0} = \frac{V^\alpha}{V_0}$	$\pi_{V^\alpha} = \frac{\partial G}{\partial b_{(V^\alpha)}} = \Pi V_0$	Swelling pressure of fibers and membranes
Electrochemical (Donnan) multiphase systems	$\sum_{k=1}^{N_s} z_k n_k^\alpha = Q^\alpha$	$\pi_{(Q^\alpha)} = \frac{\partial G}{\partial b_{(Q^\alpha)}} = F \Delta \phi^\alpha$	Process chemistry of fibers and pulps Multiphase membrane systems
Extent of reaction-controlled systems	$\sum_{k=1}^N v_{r(i),k} n_k = b_{(r_i)}$	$\pi_{(r_i)} = \frac{\partial G}{\partial b_{(r_i)}} = \frac{\partial G}{\partial \xi_i} = -\text{Aff}_i$	Paraequilibria, reactive systems
Constant contribution pH	pH = const.	$\pi_{\text{H}^{(+\text{aq})}} \equiv -RT (\text{pH}) \ln 10$	Transformed Gibbs energies in biochemical systems (pH = 7 at standard state)
Constant contribution ionic strength	$I = \frac{1}{2} \sum_k z_k^2 m_k = \text{const}$	$\pi_I \equiv \frac{-\alpha RT \sqrt{I}}{1 + B \sqrt{I}} = \frac{RT}{z_k^2} \ln \gamma_k$	Transformed Gibbs energies with constant ionic strength

$A_k$  = molar surface area of constituent

$A_0$  = unit area

$A$  = total area of system

$\sigma$  = surface energy

$V_k$  = molar surface area of constituent

$V_0$  = unit volume

$V$  = total volume of a phase or subvolume within the system

$\Pi$  = volume constraining osmotic or other pressure

$z_k$  = charge number of a species

$Q^\alpha$  = total charge of a subvolume or a phase

$F$  = Faraday constant

$\Delta \phi$  = electric potential difference for a phase

$v_{kr(i)}$  = stoichiometric coefficient for species  $k$  in reaction  $i$

$\xi_i$  = advancement of reaction  $i$

$\text{Aff}_i$  = affinity of reaction  $i$

$R$  = gas constant

$T$  = temperature

$I$  = ionic strength of aqueous solution

$m_k$  = molality of solute  $k$

$\alpha, B$  = constants related to aqueous electrolyte activity theories

$\gamma_k$  = activity coefficient of solute  $k$

## CALCULATION EXAMPLES

### Surface and interface energies of mixtures

Computation of the surface energy of liquid mixtures provides a simple introductory example of the use of immaterial constraints in the Gibbsian multicomponent systems. Existence of a surface monolayer, being in equilibrium with the bulk system (the surface curvature effects are neglected), is assumed. It is customary to separate the contributions of the bulk (*b*) and surface (*s*) contributions to the Gibbs energy as follows [23]:

$$G = \sum_{k=1}^{N_b} \mu_k^b n_k^b + \sum_{k=1}^{N_s} \mu_k^s n_k^s + \sum_{k=1}^{N_s} A_k n_k^s \quad (9)$$

where  $A_k$  is the molar surface area of species *k* and  $\sigma$  the surface tension in the system. Both the bulk and surface parts have the same constituents with the same index number *k* referring to same species in eq. 9. The respective conservation equations corresponding to the condition (eq. 2) for the equilibrium surface system are

$$\sum_{\alpha=1}^{\Omega} \sum_{k=1}^{N_{\alpha}} c_{kj}^{\alpha} n_k^{\alpha} - b_j = 0 \quad (j = 1, 2, \dots, l) \quad (10)$$

$$\sum_{\alpha=1}^{\Omega} \sum_{k=1}^{N_{\alpha}} \left( A_k^{\alpha} / A_0 \right) n_k^{\alpha} - A^{\alpha} / A_0 = 0 \quad (11)$$

Equation 10 is the mass balance equation for the components, presented in terms of the stoichiometric numbers ( $c_{kj}$ ), which appear as elements in the respective conservation matrix *C* (see, e.g., [1,3,20]). As the surface area of the equilibrium system is also a conserved quantity, eq. 11 is then

derived from the condition  $\sum_{k=1}^{N_s} A_k n_k^s = A$ , where *A* is the total surface area. To reach an analogous (dimensionless) form with the mass balance constraint (eq. 10), the unit area [ $\text{m}^2/\text{mol}$ ] normalization constant  $A_0$  has been used. The condition (eq. 11) is only applicable for the surface phase, and thus the summation over phases is irrelevant and merely shown to indicate the formal similarity of the two conditions.

When comparing eqs. 7 and 9 combined with eq. 11 one obtains for the surface energy of the mixture

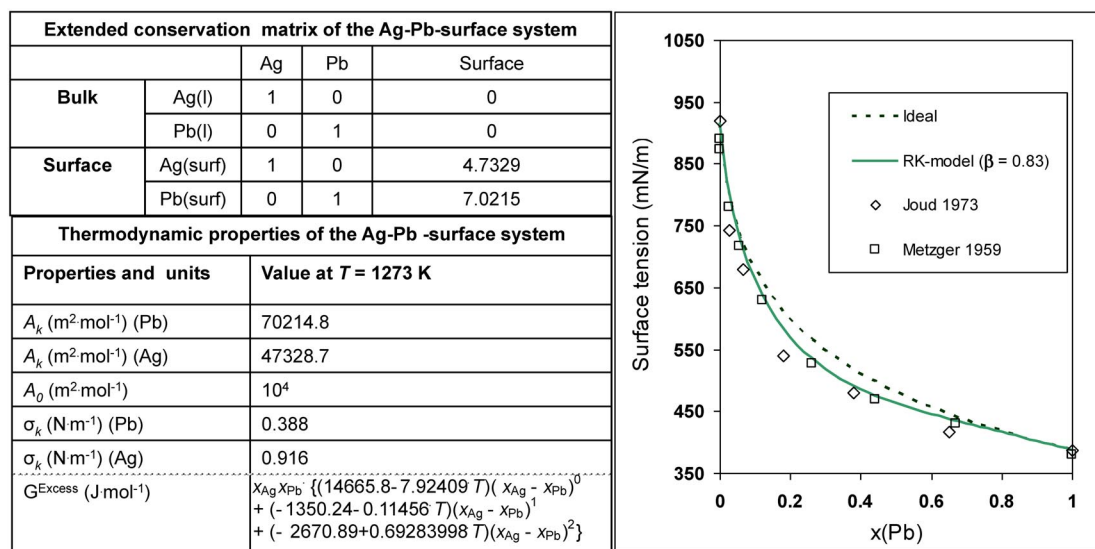
$$\sigma A_0 = \pi_{j=NC'+1} \quad (12)$$

The subscript  $j = NC' + 1$  indicates the additional immaterial “surface” component of the system. This result can also be derived from eq. 5 by using eqs. 9–11 in the minimization procedure as was shown in [25,26]. The additional elements of the conservation matrix are the  $A_k/A_0$  ratios as deduced in eq. 11. The molar surface areas of the pure substances can be derived from the respective molar volumes [27] or by using estimates of the molecular diameters ([24] p. 212). The constant  $A_0$  can be chosen arbitrarily, but for practical calculation reasons it is advantageous if the ratio  $A_k/A_0$  has a numerical value close to unity, being of the same order of magnitude as the stoichiometric coefficients appearing in the conservation matrix.

To perform the surface tension calculations with a Gibbs energy minimizing program, the input data must be arranged in terms of the standard state and excess Gibbs energy data of chemical potentials of the surface system. The relation between the appropriate standard states was originally deduced by Butler [28]

$$\mu_k^{\circ,s} = \mu_k^{\circ} + A_k \sigma_k \quad (13)$$

The necessary input for a Gibbsian surface energy calculation thus must include not only the standard state and thermodynamic activity (excess Gibbs energy) data for the constituents of the bulk and surface phases but also the data for surface tensions of the pure substances ( $\sigma_k$ ) as well as their molar surface areas ( $A_k$ ). As a simple calculation example, the melt of silver (Ag) and lead (Pb) is presented in Fig. 1. The figure shows the calculated surface tension and the composition of the surface phase in terms of the mole fraction of lead in the bulk. The excess Gibbs energy is formulated as a Redlich–Kister polynomial with parameters assessed for the Ag–Pb bulk binary system [25].



**Fig. 1** Calculation of the surface tension of a non-ideal binary system. The excess Gibbs energy ( $G^E$ ) is included as the Redlich–Kister polynomial and the  $G^E(\text{surface}) = 0.83G^E(\text{bulk})$  as deduced from the reduced coordination number between atoms in the surface region [31]. Experimental values are from [29,30].

The CFE method applies to surface and interfacial energy problems in a wide range of temperatures and mixtures ranging from binary and ternary melts to aqueous-organic and organic systems and have been further discussed, for example, in [26,32,33].

### Electrochemical Donnan-potential in multiphase systems

When two aqueous solutions at the same temperature are separated with a semi-permeable interface, which allows transport of some ions but not others, the Donnan equilibrium is formed in the system of the two compartments ([24] p. 307). The system consists of two aqueous phases with water as solvent and mobile and immobile ions as solute species. Gas as well as precipitating solids affecting the solution equilibria may yet be present. The aqueous solutions in both compartments remain electrically neutral. The essential feature of the Donnan equilibrium is that due to the macroscopic charge balance in the separate compartments, immobility of some of the ions will cause an uneven distribution also for the mobile ions. This distribution strongly depends on the acidity (pH) of the system in such cases where dissociating molecules in one of the compartments (being immobile acidic groups typically present, e.g., in the fibrils of cellulose fibers) may release mobile hydrogen ions, while their respective (large or bound) counter anions remain immobile due to the separating membrane interface or chemical bonding.

By applying the electroneutrality condition together with other physical conditions of the membrane system, the approach with immaterial constraints allows the calculation of the multiphase Donnan equilibrium with Gibbs energy minimization. Thus, the distribution of ions in the two compartments, together with, for example, formation of precipitating phases can be reproduced with a computational multiphase model.

Table 2 shows the additional immaterial constraints in the Donnan system including the electroneutrality conditions for both aqueous phases and conservation of water in the secondary aqueous compartment. Gibbs energy data for each constituent can be obtained from standard sources. The HAc/Ac<sup>-</sup> dissociation constants for the immobile acidic groups can further be transformed to  $\Delta G$  data applicable in the calculations. The activity coefficients of the solute species are obtained from an appropriate Pitzer interaction model [13,34].

**Table 2** Elements of the conservation matrix in the multicomponent Donnan equilibrium model.

		O	H	Me	...	e <sup>-</sup>	Anion <sub>a</sub>	H <sub>2</sub> O''	charge''
Solution 1	H <sub>2</sub> O	1	2						
	H <sup>+</sup>		1			-1			
	OH <sup>-</sup>	1	1			1			
	Me <sup>+</sup>			1		-1			
	⋮				⋮				
Solution 2	H <sub>2</sub> O	1	2					1	
	H <sup>+</sup>		1			-1			1
	OH <sup>-</sup>	1	1			1			-1
	Me <sup>+</sup>			1		-1			1
	⋮				⋮				
	Anion <sub>a</sub> <sup>-</sup>					1	1		-1

Assuming the same standard state of solute ions in both aqueous compartments and using the Lagrange method to solve the  $\pi_j$  values there is [35]

$$F \Delta\phi = \pi_{q''} \quad (14)$$

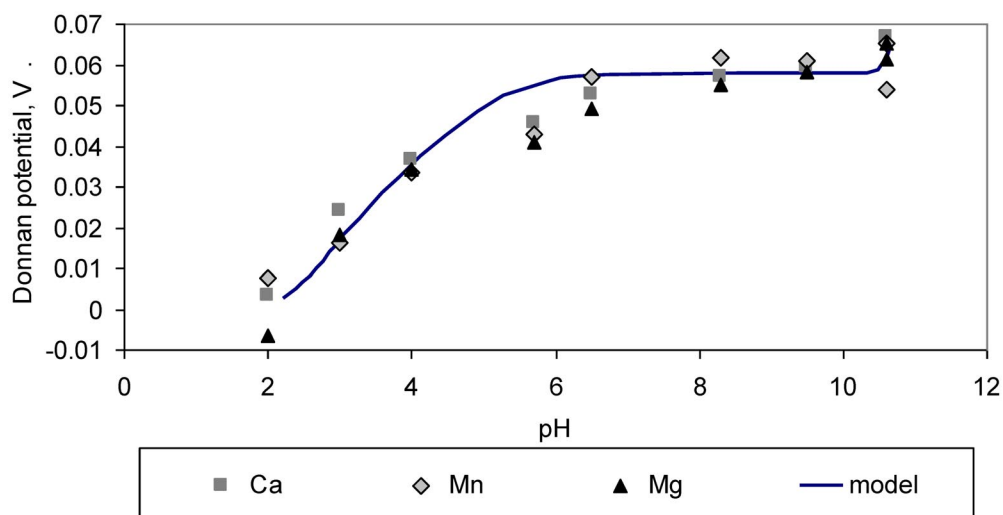
where  $\Delta\phi$  is the electrochemical potential difference between the two aqueous phases,  $F$  is Faraday constant and  $\pi_{q''}$  is the Lagrange multiplier for the immaterial charge component. Respectively, the additional constraint set for the incompressible solvent water gives

$$-\pi_{\text{H}_2\text{O}''} = RT \ln \left( \frac{a'_{\text{H}_2\text{O}}}{a''_{\text{H}_2\text{O}}} \right) = (p'' - p) V_{\text{H}_2\text{O}}^m \quad (15)$$

where the  $(p'' - p)$  factor is the osmotic pressure difference between the two liquid parts and therefore also the pressure effect required for the pulp structure to exert in order to prevent further swelling of the fibers [35].

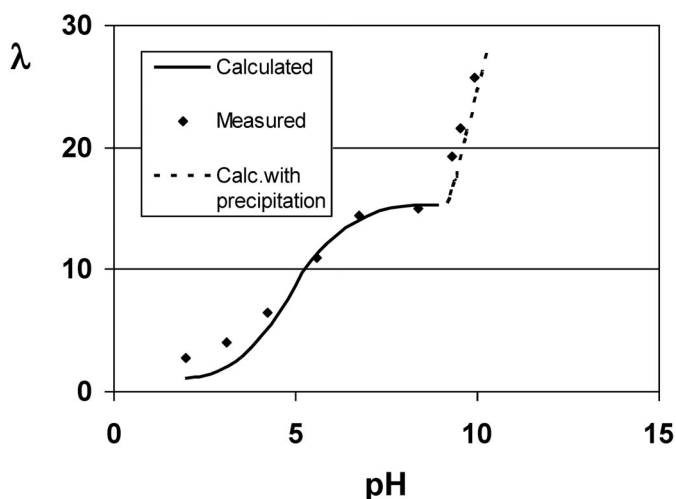
In Fig. 2, the Donnan potential calculation has been compared to the values deduced using the experimental concentration ratios of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup> ions together with modeled activity coefficients. The open symbols at high pH are calculated subtracting from the experimental fiber metal content the amounts of model predicted precipitated Mg and Mn hydroxides. The steep rise of the Donnan potential at high pH is also caused by the predicted hydroxide precipitation, as this reduces the ionic concentrations in the aqueous phases. The input data, as taken from [36], is explained in more detail in [34,35]. The advantage of the multiphase Gibbsian model is in its ability to take into account not only the multicomponent ion exchange equilibria but also other chemical and phase changes in the system.





**Fig. 2** Donnan potential in an aqueous fiber suspension as function of pH. The experimental values are deduced from the measured solute concentrations of the ions  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Mg}^{2+}$ , respectively. The result thus also indicates the non-selectivity of the ionic distribution in the Donnan system.

In Fig. 3, this is illustrated by showing the distribution of  $\text{Ca}^{2+}$  ions in an aqueous suspension of typical thermomechanical pulp. Thus, the effects of precipitating phases and that of gaseous components can be included, as well as possible reactive solute effects, such as chelants. The method has been extensively used for practical studies and process simulations of various unit processes in pulp- and paper-making [34].



**Fig. 3** The Donnan distribution coefficient (ratio of solute concentrations in the two aqueous phases) for  $\text{Ca}^{2+}$  ions in thermomechanical pulp. The continuous curve shows the range of the actual Donnan equilibrium within the salt solubility range. The dotted line has been calculated by including the precipitated calcium ( $\text{CaCO}_3$ ) in the nominator of the distribution coefficient. This is in agreement with the experimental observation, as the Ca precipitate nucleates onto the fibers and is thus analyzed from the fiber samples.

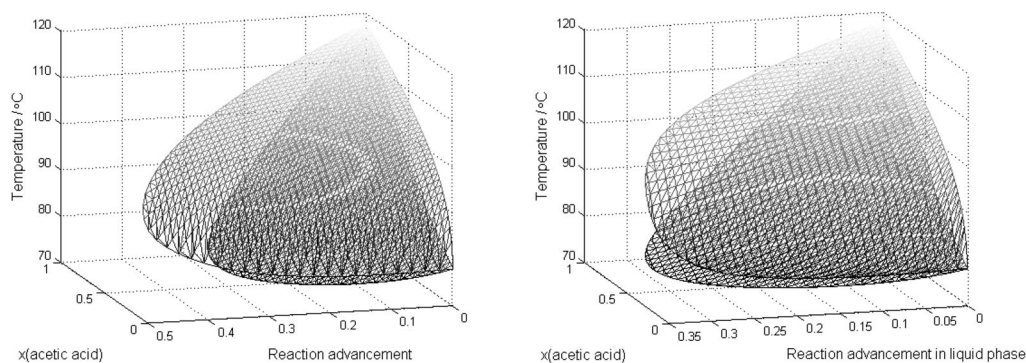
### Systems constrained by the extent of reaction

As shown with the above examples, the CFE minimization generally results in another undetermined Lagrange multiplier, which gives the desired property as a constraint potential. The same technique can be used for a fixed amount of a virtual system component, which then serves to limit the time-dependent extent of a selected chemical reaction or phase change. The additional Lagrange multipliers then appear as the non-zero affinities of the kinetically constrained non-equilibrium reactions [20,37]. This feature enables the use of the Gibbsian multiphase method effectively, e.g., in the simulation of various chemical and combustion processes [38–40]. Such applications often include mass and heat transfer models and other process-specific features which are beyond the scope of this text. From the thermodynamic point of view, an appropriate example is, however, the construction of reactive phase diagrams for systems where the chemical change appears at a given (non-equilibrium) extent of reaction, while the respective phase composition is at equilibrium.

Chemical reaction kinetics can often prevent equilibration in chemically reactive fluid mixtures, particularly at low temperatures and in conditions where the phase separation is to take place in a short residence time [41]. The well-known ethanol-acetic acid, water-ethylacetate system serves as a viable example [42] and was chosen to illustrate the respective calculation by using the constrained Gibbs energy technique.

As physical components of the model system, those corresponding to ethanol, acetic acid, and water were selected. Yet, the same result can be obtained with the elements (C, H, and O) as physical components. Additional immaterial constraint was applied to the ethyl acetate species allowing the control of the advancement of the esterification reaction. The standard-state chemical potentials from [43] were adjusted by using the vapor pressure data from several sources [44–47]. The vapor phase was regarded as an ideal gas including the acetic acid dimer, while the liquid mixture is modeled using the UNIFAC data [48].

Dew and bubble temperatures plotted in terms of the feed composition and reaction advancement as two-dimensional surfaces are shown in Fig. 4 (left). For depicting vapor–liquid equilibria, it is more relevant to compare the vapor and liquid phase not with the same reaction advancement of the esterification reaction, but the two phases with equal affinity for the reaction [41]. It is straightforward to perform the respective isoaffinity calculation, as in the CFE method the Lagrange multiplier adjacent to the extent of a kinetically constrained reaction provides directly the non-equilibrium affinity [37,49]. The result is shown in Fig. 4 (right) where one of the coordinates is the advancement of the reaction in the liquid phase.



**Fig. 4** Dew and bubble point surfaces for the reactive ethanol acetic acid system. The chemical reaction is the esterification of acetic acid with ethanol:  $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{H}_2\text{O}$ . The graphs are produced by using one of the axis either as reaction advancement (left) or as reaction advancement in the liquid phase together with isoaffinity condition (right).

## CONCLUSION

The use of immaterial and virtual constraints provides a thermodynamically consistent extension of the Gibbs energy minimization calculation for multiphase systems. Adjusting the thermodynamic system for constrained Gibbs energy calculations appears mathematically identical to the procedure involved in the conventional Gibbsian equilibrium calculations. The immaterial constraints must be defined in advance for the calculation system and be included as parts of the conservation matrix. The immaterial constraints and their conjugate potentials are principally those which may appear in the generalized Gibbs energy function or, alternatively, may be derived from it by using the appropriate Legendre transform. Within a few years, the new method has found applications in solving surface and interfacial energies of mixtures, electrochemical potentials of membrane systems, and non-equilibrium affinities for reactive systems. The consistent thermodynamic basis of the method suggests that new interesting topics may appear in various fields of process chemistry and materials science as well as in, for example, biochemical pathway analysis.

## REFERENCES

1. W. R. Smith, R. W. Missen. *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*, Krieger, Malabar, FL (1991).
2. S. Gordon, B. J. McBride. *Computer Program for Calculation of Complex Equilibrium Compositions and Applications*, NASA Reference Publication 1311 (1994).
3. G. Eriksson. *Acta Chem. Scand.* **25**, 2651 (1971).
4. M. Hillert. *Bull. Alloy Phase Diagrams* **2**, 265 (1981).
5. L. Kaufman, H. Bernstein. *Computer Calculation of Phase Diagrams*, Academic Press, New York (1970).
6. K. Hack (Ed.). *The SGTE Casebook: Thermodynamics at Work*, 2<sup>nd</sup> ed., p. 14, Woodhead, Cambridge (2008).
7. S. M. Walas. *Phase Equilibria in Chemical Engineering*, Butterworth, Stoneham, MA (1985).
8. A. L. Ballard, E. D. Sloan. *Fluid Phase Equilib.* **218**, 15 (2004).
9. D. V. Nichita, S. Gomez, E. Luna. *Comput. Chem. Eng.* **26**, 1703 (2002).
10. E. Königsberger, G. Eriksson. *J. Solution Chem.* **28**, 721 (1998).
11. E. Königsberger. *Pure Appl. Chem.* **74**, 1831 (2002).
12. J. Lindgren, L. Wiklund, L.-O. Öhman. *Nordic Pulp Paper Res. J.* **16**, 24 (2001).
13. P. Koukkari, R. Pajarre, H. Pakarinen. *J. Solution Chem.* **31**, 627 (2002).
14. P. Sundman, P. Persson, L.-O. Öhman. *J. Colloid Interface Sci.* **328**, 248 (2008).
15. M. Lampinen, J. Vuorisalo. *J. Electrochem. Soc.* **139**, 484 (1992).
16. R. A. Alberty. *J. Phys. Chem.* **93**, 3299 (1989).
17. J. C. Keck, D. Gillespie. *Combust. Flame* **17**, 237 (1971).
18. J. C. Keck. *Prog. Energy Combust. Sci.* **16**, 125 (1990).
19. P. Koukkari. *Comput. Chem. Eng.* **17**, 1157 (1993).
20. P. Koukkari, R. Pajarre. *CALPHAD* **30**, 18 (2006).
21. R. Pajarre, P. Blomberg, P. Koukkari. *Comput.-Aided Chem. Eng.* **25**, 883 (2008).
22. P. B. A. Blomberg, P. Koukkari. *Math. Biosci.* **220**, 81 (2009).
23. R. Alberty. *Pure Appl. Chem.* **73**, 1349 (2001).
24. E. A. Guggenheim. *Thermodynamics*, p. 335, North-Holland, Amsterdam (1977).
25. P. Koukkari, R. Pajarre, K. Hack. *Int. J. Mater. Res.* **98**, 926 (2007).
26. R. Pajarre, P. Koukkari, T. Tanaka, Y. Lee. *CALPHAD* **30**, 196 (2006).
27. E. T. Turkdogan. *Physical Chemistry of High-Temperature Technology*, p. 96, Academic Press, London (1980).
28. J. A. V. Butler. *Proc. R. Soc., London, A* **135**, 348 (1932).

29. J. C. Joud, N. Eustathopoulos, P. Desse. *J. Chim. Phys.* **70**, 1290 (1973).
30. G. Metzger. *Z. Phys. Chem.* **211**, 1 (1959).
31. T. Tanaka, K. Hack, T. Ida, S. Hara. *Z. Metallkunde* **87**, 380 (1996).
32. R. Pajarre, P. Koukkari. *J. Colloid Interface Sci.* **337**, 39 (2009).
33. R. Pajarre, P. Koukkari, T. Tanaka. To be published.
34. P. Koukkari, R. Pajarre, E. Räsänen. In *Chemical Thermodynamics for Industry*, T. M. Letcher (Ed.), pp. 23–32, Royal Society of Chemistry, Cambridge, UK (2004).
35. R. Pajarre, P. Koukkari, E. Räsänen. *J. Mol. Liq.* **125**, 58 (2006).
36. M. Towers, A. M. Scallan. *J. Pulp Paper Sci.* **22**, J332 (1996).
37. P. Koukkari, R. Pajarre, P. Blomberg. *Pure Appl. Chem.* **83**, 1063 (2011).
38. P. Koukkari, I. Laukkanen, S. Liukkonen. *Fluid Phase Equilib.* **136**, 345 (1997).
39. M. Janbozorgi, S. Ugarte, H. Metghalchi, J. C. Keck. *Combust. Flame* **156**, 1871 (2009).
40. R. Gani, T. S. Jepsen, E. S. Pérez-Cisneros. *Comput. Chem. Eng.* **22**, Suppl., S363 (1998).
41. G. Maurer. *Fluid Phase Equilib.* **116**, 39 (1996).
42. A. Toikka, M. Toikka, Yu. Pisarenko, L. Serafimov. *Theor. Found. Chem. Eng.* **43**, 129 (2009).
43. A. Roine, Outokumpu. *HSC Chemistry® for Windows*, Version 4.1 (1999).
44. A. C. Vawdrey, J. L. Oscarson, R. L. Rowley, W. V. Wilding. *Fluid Phase Equilib.* **222–223**, 239 (2004).
45. D. Ambrose, J. H. Ellender, C. H. S. Sprake, R. Townsend. *J. Chem. Thermodyn.* **9**, 735 (1977).
46. P. Sauermann, K. Holzapfel, J. Oprzynski, F. Kohler, W. Poot, T. W. de Loos. *Fluid Phase Equilib.* **112**, 249 (1995).
47. H. S. Wu, S. I. Sandler. *J. Chem. Eng. Data* **33**, 157 (1988).
48. B. E. Poling, J. M. Prausnitz, J. M. O'Connell. *Properties of Gases and Liquids*, 5<sup>th</sup> ed., McGraw-Hill (2001).
49. P. Koukkari, R. Pajarre. *Comput. Chem. Eng.* **30**, 1189 (2006).