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C. R. Acad. Sci. Paris, Ser. I 340 (2005) 765–768
COMPTES RENDUS MATHEMATIQUE
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Numerical Analysis

An optimization problem related to the modeling of atmospheric organic aerosols

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Received 2 January 2005; accepted 25 January 2005

Available online 4 May 2005

Presented by Roland Glowinski

Abstract

A mathematical model for the computation of the phase equilibrium related to atmospheric organic aerosols is proposed. The equilibrium is given by the minimum of the Gibbs free energy and is characterized using the notion of phase simplex of its convex hull. A primal-dual interior-point method solving the *Karush–Kuhn–Tucker* conditions is detailed. Numerical results show the efficiency of our algorithm. ***To cite this article: N.R. Amundson et al., C. R. Acad. Sci. Paris, Ser. I 340 (2005).***

Résumé

Un problème d'optimisation lié à la modélisation d'aérosols organiques. Nous proposons un modèle pour l'étude de l'équilibre chimique lié à la modélisation d'aérosols organiques. L'état d'équilibre est caractérisé par le minimum global d'énergie de Gibbs et décrit par le « simplexe de phases » de son enveloppe convexe. Nous présentons une méthode de point intérieur pour la résolution du système formé par les conditions de *Karush–Kuhn–Tucker*. Des résultats numériques montrent l'efficacité de notre algorithme. ***Pour citer cet article : N.R. Amundson et al., C. R. Acad. Sci. Paris, Ser. I 340 (2005).***

In this Note, the problem of phase equilibrium for organic aerosols is addressed. This problem requires the accurate identification of the existing phases at the equilibrium for a closed system. This equilibrium state is characterized by the global minimum of the Gibbs free energy for the system. This problem is equivalent to the

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[1] Supported by the Swiss National Science Foundation, Grant PBEL2-103152.

[2] Supported by the United States Environmental Protection Agency through Cooperative Agreement CR-829068-01 to the University of Houston.

1631-073X/$ – see front matter
doi:10.1016/j.crma.2005.04.018

determination of the convex hull of the corresponding molar Gibbs energy function. A mathematical analysis of the convex hull is presented using a geometrical concept of phase simplex. A primal-dual interior-point algorithm for the efficient solution of the phase equilibrium problem is proposed. The algorithm applies at each step a Newton method to the Karush–Kuhn–Tucker (KKT) system of equations, perturbed by a log-barrier penalty term, to find the next primal-dual approximation of the solution. This local approach is used for the determination of the global minimum of the Gibbs free energy by using a novel initialization strategy based on the properties of phase simplexes. Starting from an initial solution involving all possible phases in the system, the algorithm allows to identify the vanishing phases at the equilibrium. Numerical results show the robustness and accuracy of the approach.

The phase equilibrium for a system of n_s substances at a specified temperature T and pressure P and for a given substance-abundance vector in units of moles $\mathbf{b} \in \mathbb{R}^{n_s}_{++}$ (i.e., $> \mathbf{0}$) is the solution of the constrained minimization problem

$$\min \sum_{\alpha=1}^{\pi} y_\alpha g(\mathbf{x}_\alpha), \quad \text{s.t.} \quad \mathbf{x}_\alpha \in \Delta'_{n_s},\ y_\alpha \geqslant 0,\ \sum_{\alpha=1}^{\pi} y_\alpha \mathbf{x}_\alpha = \mathbf{b}, \tag{1}$$

where $\Delta'_{n_s} = \{\mathbf{x} \in \mathbb{R}^{n_s}\colon\ \mathbf{e}^{\mathrm{T}}\mathbf{x} = 1,\ \mathbf{x} \geqslant \mathbf{0}\}$ with $\mathbf{e}^{\mathrm{T}} = (1, \ldots, 1)$, π is the number of possible phases, $\mathbf{x}_\alpha$ is the mole-fraction concentration vector in phase α, y_α is the total number of moles in phase α, and g is the molar Gibbs free energy function. It is assumed that g is C^∞ in $\mathbb{R}^{n_s}_{++}$, its values approach finite limits as any given mole fraction tends to zero, and these limiting values are approached with negatively infinite slope.

Let $n = n_s - 1$, define $\Delta_n = \{\mathbf{z} \in \mathbb{R}^n\colon\ \mathbf{e}^{\mathrm{T}}\mathbf{z} \leqslant 1,\ \mathbf{z} \geqslant 0\}$, and denote by $\operatorname{int}\Delta_n$ its interior. Note that Δ_n is the unit simplex in $\mathbb{R}^n$, i.e., $\Delta_n = \operatorname{conv}(\mathbf{e}_0, \mathbf{e}_1, \ldots, \mathbf{e}_n)$ with $\mathbf{e}_0 = \mathbf{0}$ and $\{\mathbf{e}_1, \ldots, \mathbf{e}_n\}$ being the canonical basis. The simplex Δ_n can be identified with Δ'_{n_s} via the mapping $\Pi : \Delta_n \ni \mathbf{z} \mapsto \mathbf{x} = \mathbf{e}_{n_s} + \mathbf{Z}_{\mathbf{e}}\mathbf{z} \in \Delta'_{n_s}$ where $\mathbf{Z}^{\mathrm{T}}_{\mathbf{e}} = (\mathbf{I}, -\mathbf{e})$ with $\mathbf{I}$ the identity matrix. Let $f = g \circ \Pi$. Then, f is C^0 on Δ_n, C^∞ on $\operatorname{int}\Delta_n$, and has the subdifferential $\partial f(\mathbf{z}) = \emptyset$ for $\mathbf{z} \in \partial\Delta_n$. Let $\mathbf{b}$ be scaled so that $\mathbf{e}^{\mathrm{T}}\mathbf{b} = 1$ and define $\mathbf{d} = \Pi^{-1}(\mathbf{b})$. The fact of $\mathbf{b}$ being in the relative interior of Δ'_{n_s}, denoted by $\operatorname{rint}\Delta'_{n_s}$, implies that $\mathbf{d} \in \operatorname{int}\Delta_n$. Let f be extended by ∞ outside Δ_n and denote by $\operatorname{conv} f$ the convex hull of f. According to the *Carathéodory theorem* [5], we have, for $\mathbf{d} \in \operatorname{int}\Delta_n$,

$$\operatorname{conv} f(\mathbf{d}) = \min \sum_{\alpha=1}^{\pi} y_\alpha f(\mathbf{z}_\alpha), \quad \text{s.t.} \quad \mathbf{z}_\alpha \in \Delta_n,\ y_\alpha \geqslant 0,\ \sum_{\alpha=1}^{\pi} y_\alpha = 1,\ \sum_{\alpha=1}^{\pi} y_\alpha \mathbf{z}_\alpha = \mathbf{d}. \tag{2}$$

Problem (2) is equivalent to (1). Theorem 1, characterizing the geometrical structure of $\operatorname{conv} f$, is based on the assumption that f is in some residual set of $C^\infty(\operatorname{int}\Delta_n)$ and on the generic properties of f [4].

Theorem 1. *For any $\mathbf{d} \in \operatorname{int}\Delta_n$, there exists a unique $(\pi - 1)$-simplex $\Sigma(\mathbf{d}) = \operatorname{conv}(\mathbf{z}_1, \ldots, \mathbf{z}_\pi)$ with $\pi \leqslant n + 1$ vertices $\mathbf{z}_\alpha \in \operatorname{int}\Delta_n$ such that $\mathbf{d} \in \operatorname{rint}\Sigma(\mathbf{d})$ and $\operatorname{conv} f(\mathbf{d}) = \sum_{\alpha=1}^{\pi} y_\alpha f(\mathbf{z}_\alpha)$ with the barycentric representation $\mathbf{d} = \sum_{\alpha=1}^{\pi} y_\alpha \mathbf{z}_\alpha$, $\sum_{\alpha=1}^{\pi} y_\alpha = 1$, and $y_\alpha > 0$.*

The $(\pi - 1)$-simplex $\Sigma(\mathbf{d}) = \operatorname{conv}(\mathbf{z}_1, \ldots, \mathbf{z}_\pi)$ is called the phase simplex of $\mathbf{d}$. Note that $\Sigma(\boldsymbol{\delta}) = \Sigma(\mathbf{d})$ for $\forall \boldsymbol{\delta} \in \operatorname{rint}\Sigma(\mathbf{d})$. Theorem 2 is related to the so-called Gibbs tangent plane criterion, which states that the affine hyperplane tangent to the graph of f at $(\mathbf{z}_\alpha, f(\mathbf{z}_\alpha))$, $\alpha = 1, \ldots, \pi$, lies entirely below the graph.

Theorem 2. *A $(\pi - 1)$-simplex $\Sigma = \operatorname{conv}(\mathbf{z}_1, \ldots, \mathbf{z}_\pi)$ is a phase simplex if and only if there exist multipliers $\boldsymbol{\eta} \in \mathbb{R}^n$ and $\xi \in \mathbb{R}$ such that*

$$\nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta} = \mathbf{0}, \qquad \forall \alpha = 1, \ldots, \pi, \tag{3}$$

$$f(\mathbf{z}_\alpha) + \boldsymbol{\eta}^{\mathrm{T}}\mathbf{z}_\alpha + \xi = 0, \quad \forall \alpha = 1, \ldots, \pi, \tag{4}$$

$$f(\mathbf{z}) + \boldsymbol{\eta}^{\mathrm{T}}\mathbf{z} + \xi \geqslant 0, \qquad \forall \mathbf{z} \in \Delta_n. \tag{5}$$

Let $\Omega_0 = \{\mathbf{d} \in \operatorname{int} \Delta_n\colon \dim(\Sigma(\mathbf{d})) = 0\}$ be the set of single-phase points in $\operatorname{int} \Delta_n$. A point $\mathbf{d} \in \operatorname{int} \Delta_n$ is a single-phase point if and only if $\operatorname{conv} f(\mathbf{d}) = f(\mathbf{d})$. Note that the vertices of a phase simplex are single-phase points. Corollary 3 is the basis for a primal-dual formulation of problem (2).

Corollary 3. *Let $\Sigma = \operatorname{conv}(\mathbf{z}_1, \ldots, \mathbf{z}_\pi)$ be a $(\pi-1)$-simplex with $\mathbf{z}_\alpha \in \Omega_0$. If there exist multipliers $\boldsymbol{\eta} \in \mathbb{R}^n$ and $\xi \in \mathbb{R}$ satisfying conditions* (3) *and* (4)*, then Σ is a phase simplex.*

Note that each vertex $\mathbf{e}_i$, $i = 0, \ldots, n$, of the unit simplex Δ_n corresponds to the single-phase point of a pure substance system; for a neighborhood $\mathcal{V}_i \in \mathcal{N}(\mathbf{e}_i)$, define $\mathcal{V}_i^0 = \mathcal{V} \cap \Omega_0$ $(\neq \emptyset)$. Corollary 4 permits to construct, via an interior method, a sequence of n-simplexes $\mathcal{S} = \operatorname{conv}(\mathbf{d}_0, \ldots, \mathbf{d}_n)$ with $\mathbf{d}_i \in \Omega_0$ such that a $(\pi-1)$-face of $\mathcal{S}$ converges to a phase simplex $\Sigma = \operatorname{conv}(\mathbf{z}_1, \ldots, \mathbf{z}_\pi)$

Corollary 4. *For each vertex $\mathbf{z}_\alpha$, $\alpha = 1, \ldots, \pi$, of a phase simplex $\Sigma = \operatorname{conv}(\mathbf{z}_1, \ldots, \mathbf{z}_\pi)$, there exists a set $\mathcal{V}_i^0$, $i = 0, \ldots, n$, such that $\mathbf{z}_\alpha$ is connected to a point $\mathbf{d}_i^0 \in \mathcal{V}_i^0$ by a continuous path in Ω_0.*

The initialization of $\mathcal{S}$ in the algorithm below is given by $\mathcal{S}_0 = \operatorname{conv}(\mathbf{d}_0^0, \ldots, \mathbf{d}_n^0)$ with $\mathbf{d}_i^0 \in \mathcal{V}_i^0$.

In the primal-dual interior-point algorithm, (1) is first transformed into the following barrier problem:

$$\min \sum_{\alpha=1}^{\pi} y_\alpha g(\mathbf{x}_\alpha) - \nu \sum_{\alpha=1}^{\pi} \ln s_\alpha, \quad \text{s.t.} \quad \mathbf{x}_\alpha \in \operatorname{rint} \Delta'_{n_s},\ y_\alpha - s_\alpha = 0,\ s_\alpha > 0,\ \sum_{\alpha=1}^{\pi} y_\alpha \mathbf{x}_\alpha = \mathbf{b}, \tag{6}$$

where ν is a positive parameter. Problem (6) is approximately solved by applying one Newton iteration to its KKT system of equations:

$$\begin{aligned} &y_\alpha\big(\nabla g(\mathbf{x}_\alpha) + \boldsymbol{\lambda}\big) + \zeta_\alpha \mathbf{e} = \mathbf{0}, \quad g(\mathbf{x}_\alpha) + \boldsymbol{\lambda}^{\mathrm{T}} \mathbf{x}_\alpha - \theta_\alpha = 0, \quad \mathbf{e}^{\mathrm{T}} \mathbf{x}_\alpha = 1, \quad \mathbf{x}_\alpha > 0, \quad \alpha = 1, \ldots, \pi, \\ &\sum_{\alpha=1}^{\pi} y_\alpha \mathbf{x}_\alpha = \mathbf{b}, \quad y_\alpha \theta_\alpha - \nu = 0, \quad y_\alpha > 0, \quad \theta_\alpha > 0, \quad \alpha = 1, \ldots, \pi, \end{aligned} \tag{7}$$

then decreasing ν, and repeating the process. Applying Newton's method to (7) gives the following symmetric indefinite system:

$$y_\alpha \nabla^2 g(\mathbf{x}_\alpha) \mathbf{p}_{\mathbf{x}_\alpha} + \big(\nabla g(\mathbf{x}_\alpha) + \boldsymbol{\lambda}\big) p_{y_\alpha} + y_\alpha \mathbf{p}_{\boldsymbol{\lambda}} + p_{\zeta_\alpha} \mathbf{e} = -y_\alpha \nabla g(\mathbf{x}_\alpha) - y_\alpha \boldsymbol{\lambda} - \zeta_\alpha \mathbf{e}, \quad \alpha = 1, \ldots, \pi, \tag{8}$$

$$\big(\nabla g(\mathbf{x}_\alpha) + \boldsymbol{\lambda}\big)^{\mathrm{T}} \mathbf{p}_{\mathbf{x}_\alpha} + \mathbf{x}_\alpha^{\mathrm{T}} \mathbf{p}_{\boldsymbol{\lambda}} + \theta_\alpha y_\alpha^{-1} p_{y_\alpha} = -g(\mathbf{x}_\alpha) - \mathbf{x}_\alpha^{\mathrm{T}} \boldsymbol{\lambda} + \nu y_\alpha^{-1}, \quad \alpha = 1, \ldots, \pi, \tag{9}$$

$$\mathbf{e}^{\mathrm{T}} \mathbf{p}_{\mathbf{x}_\alpha} = 1 - \mathbf{e}^{\mathrm{T}} \mathbf{x}_\alpha, \quad \alpha = 1, \ldots, \pi, \tag{10}$$

$$\sum_{\alpha=1}^{\pi} y_\alpha \mathbf{p}_{\mathbf{x}_\alpha} + \sum_{\alpha=1}^{\pi} \mathbf{x}_\alpha\, p_{y_\alpha} = \mathbf{b} - \sum_{\alpha=1}^{\pi} y_\alpha \mathbf{x}_\alpha. \tag{11}$$

The iterates are then updated by $y_\alpha^+ = y_\alpha + \tau p_{y_\alpha}$, $\mathbf{x}_\alpha^+ = \mathbf{x}_\alpha + \tau \mathbf{p}_{\mathbf{x}_\alpha}$, $\zeta_\alpha^+ = \zeta_\alpha + \tau p_{\zeta_\alpha}$, $\theta_\alpha^+ = \theta_\alpha + \tau p_{\theta_\alpha}$, for $\alpha = 1, \ldots, \pi$, and $\boldsymbol{\lambda}^+ = \boldsymbol{\lambda} + \tau \mathbf{p}_{\boldsymbol{\lambda}}$, where the step-size τ is chosen to ensure that $y_\alpha^+ > 0$ and $\theta_\alpha^+ > 0$, and a merit function associated to (6) is sufficiently reduced. To ensure that this sequence of iterates converges to the global minimizer of (1) as $\nu \to 0$, (8)–(11) is projected onto the null-space $\mathcal{Z}_e = \{\mathbf{p}_{\mathbf{x}} \in \mathbb{R}^{n_s}\colon \mathbf{e}^{\mathrm{T}} \mathbf{p}_{\mathbf{x}} = 0\}$ to obtain:

$$y_\alpha \nabla^2 f(\mathbf{z}_\alpha) \mathbf{p}_{\mathbf{z}_\alpha} + \big(\nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta}\big) p_{y_\alpha} + y_\alpha \mathbf{p}_{\boldsymbol{\eta}} = \mathbf{r}_{\mathbf{z}_\alpha}, \quad \alpha = 1, \ldots, \pi, \tag{12}$$

$$\big(\nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta}\big)^{\mathrm{T}} \mathbf{p}_{\mathbf{z}_\alpha} + \mathbf{z}_\alpha^{\mathrm{T}} \mathbf{p}_{\boldsymbol{\eta}} + (\mathbf{e}^{\mathrm{T}} \mathbf{x}_\alpha) p_\xi + \theta_\alpha y_\alpha^{-1} p_{y_\alpha} = r_{y_\alpha}, \quad \alpha = 1, \ldots, \pi, \tag{13}$$

$$\sum_{\alpha=1}^{\pi} y_\alpha \mathbf{p}_{\mathbf{z}_\alpha} + \sum_{\alpha=1}^{\pi} \mathbf{z}_\alpha p_{y_\alpha} = \mathbf{r}_{\boldsymbol{\eta}}, \qquad \sum_{\alpha=1}^{\pi} (\mathbf{e}^{\mathrm{T}} \mathbf{x}_\alpha) p_{y_\alpha} = r_\xi, \tag{14}$$

Table 1
Phase equilibrium states for several chemical systems available in the literature, together with feed vectors, total number of iterations for convergence and value of the Gibbs energy. Example 5 is given with data extracted from [a] [1] and [b] [2]

	Feed vector			Phase 1			y_1	Phase 2			y_2	Phase 3			y_3	# iter	Gibbs energy
[3] example 4	0.4	0.1	0.5	0.349	0.426	0.224	0.2153	0.101	0.009	0.889	0.4949	0.948	0.013	0.039	0.2898	44	−0.13109
[3] example 5[a]	0.588	0.118	0.294	0.022	0.957	0.021	0.0001	0.003	0.070	0.927	0.3169	0.859	0.139	0.001	0.6829	18	−0.10256
[3] example 5[b]	0.588	0.118	0.294	0.053	0.188	0.759	0.3867	0.926	0.073	0.001	0.6133	–	–	–	–	20	−0.19587
[3] example 6	0.4	0.2	0.4	0.028	0.162	0.810	0.4826	0.747	0.236	0.017	0.5174	–	–	–	–	16	−0.29043
[3] example 7	0.62	0.08	0.3	0.311	0.125	0.564	0.5194	0.954	0.031	0.014	0.4806	–	–	–	–	20	−0.27752
[3] example 9	0.6	0.2	0.2	0.314	0.348	0.337	0.4574	0.841	0.075	0.084	0.5426	–	–	–	–	22	−0.39882
[3] example 11	0.1	0.3	0.6	0.119	0.513	0.368	0.5087	0.080	0.079	0.840	0.4913	–	–	–	–	16	−0.28494

where $\mathbf{d}$ is the n first components of $\mathbf{b}$, $\boldsymbol{\eta} = \mathbf{Z}_{\mathbf{e}}^{\mathrm{T}}\boldsymbol{\lambda}$, $\xi = \mathbf{e}_{n_s}^{\mathrm{T}}\boldsymbol{\lambda}$, for $\alpha = 1, \ldots, \pi$, $\mathbf{z}_\alpha$ is the n first components of $\mathbf{x}_\alpha$, $\nabla f(\mathbf{z}_\alpha) = \mathbf{Z}_{\mathbf{e}}^{\mathrm{T}}\nabla g(\mathbf{x}_\alpha)$, $\nabla^2 f(\mathbf{z}_\alpha) = \mathbf{Z}_{\mathbf{e}}^{\mathrm{T}}\nabla^2 g(\mathbf{x}_\alpha)\mathbf{Z}_{\mathbf{e}}$, $\mathbf{r}_{\mathbf{z}_\alpha} = -y_\alpha \nabla f(\mathbf{z}_\alpha) - y_\alpha \boldsymbol{\eta} - y_\alpha(1 - \mathbf{e}^{\mathrm{T}}\mathbf{x}_\alpha)(\boldsymbol{\partial}^2_{1:n,n_s} g(\mathbf{x}_\alpha) - \partial^2_{n_s,n_s} g(\mathbf{x}_\alpha)\,\mathbf{e})$, $r_{y_\alpha} = -g(\mathbf{x}_\alpha) - \mathbf{x}_\alpha^{\mathrm{T}}\boldsymbol{\lambda} + \nu y_\alpha^{-1} - (1 - \mathbf{e}^{\mathrm{T}}\mathbf{x}_\alpha)(\partial_{n_s} g(\mathbf{x}_\alpha) + \xi)$, $\mathbf{r}_{\boldsymbol{\eta}} = \mathbf{d} - \sum_{\alpha=1}^{\pi} y_\alpha \mathbf{z}_\alpha$, and $r_\xi = \mathbf{e}^{\mathrm{T}}\mathbf{b} - \sum_{\alpha=1}^{\pi} y_\alpha$. The solvability of (12)–(14) is given in Theorem 5.

Theorem 5. *If* $\mathrm{conv}(\mathbf{z}_1, \ldots, \mathbf{z}_\pi)$ *is a* $(\pi - 1)$*-simplex and* $\mathbf{z}_\alpha \in \Omega_0$ *for* $\forall \alpha = 1, \ldots, \pi$*, the linear system* (12)–(14) *has a unique solution. Moreover, if* $\nabla^2 f(\mathbf{z}_\alpha)$*, for* $\forall \alpha = 1, \ldots, \pi$*, is positive definite,* (12)–(14) *is solvable by a range-space method based on the Schur complement.*

We have the following convergence theorem for the primal-dual interior-point algorithm.

Theorem 6. *Let* $\{y_\alpha^\dagger, \mathbf{z}_\alpha^\dagger\}_{\alpha=1,\pi^\dagger}$ *be the solution of* (2) *for a point* $\mathbf{d} \in \mathrm{int}\,\Delta_n$ *with* $\mathbf{d} = \sum_{\alpha=1}^{\pi^\dagger} y_\alpha^\dagger \mathbf{z}_\alpha^\dagger$*. Assume* $\pi = n+1$ *and let* $\{y_i^\nu, \mathbf{z}_i^\nu\}_{i=1,\pi}$ *be the sequence of iterates generated by algorithm* (12)–(14) *and define* $\mathbf{d}^\nu = \sum_{i=1}^{\pi} y_i^\nu \mathbf{z}_i^\nu$*. If the sequence* $\mathcal{S}^\nu = \mathrm{conv}(\mathbf{z}_1^\nu, \ldots, \mathbf{z}_\pi^\nu)$ *is initialized by* $\mathcal{S}_0$ *and remains as* $(\pi - 1)$*-simplexes with* $\mathbf{z}_i^\nu \in \Omega_0$*, then, as* $\nu \to 0$, $\mathbf{d}^\nu \to \mathbf{d}$*. Furthermore, for* $\forall \alpha = 1, \ldots, \pi^\dagger$*, there is a unique* $i(\alpha) \in \{1, \ldots, \pi\}$ *such that* $y_{i(\alpha)}^\nu \to y_\alpha^\dagger$ *and* $\mathbf{z}_{i(\alpha)}^\nu \to \mathbf{z}_\alpha^\dagger$*; for* $j \in \{1, \ldots, \pi\} \setminus \{i(\alpha)\}_{\alpha=1,\pi^\dagger}$, $y_j^\nu \to 0$.

This convergent sequence is used for a finite termination of the algorithm by identifying the vanishing phases, i.e. the phases $i \in \{1, \ldots, \pi\}$ such that $y_i \leqslant \varepsilon$, where ε is a given *a priori* tolerance.

The chemical systems considered here are extracted from [3]. These examples involve $n_s = 3$ substances and thus a maximum of three phases at equilibrium. Table 1 gives the equilibrium states $\{\mathbf{x}_\alpha^\dagger, y_\alpha^\dagger\}$ of these systems obtained with our algorithm for a given feed vector $\mathbf{b}$, the total number of iterations for convergence and the value of the Gibbs energy. The algorithm is initialized with $\pi = n + 1$ and $\mathcal{S} = \mathcal{S}_0$. The initial value ν^0 is given by 10^{-3} and the tolerance ε for eliminating the vanishing phases is 10^{-8}. The penalty parameter is updated with $\nu^{k+1} = 0.7 \cdot \nu^k$ and one iteration of the Newton method is carried out for each value ν^k. The iterations are stopped when the relative error between the iterates for ν^k and ν^{k+1} is 10^{-3}. Results compare well with those reported in [3], where a global optimization method was used, and here, for all cases, the convergence is fast, i.e., achieved in less than 50 iterations.

References

[1] A. Fredenslund, J. Gmehling, P. Rasmussen, Vapor–Liquid Equilibrium Using UNIFAC, Elsevier, Amsterdam, 1977.
[2] T. Magnussen, P. Rasmussen, A. Fredenslund, UNIFAC parameter table for prediction of liquid–liquid equilibria, Industrial and Engineering Chemistry Process Design and Development 20 (1981) 331–339.
[3] C.M. McDonald, C.A. Floudas, GLOPEQ: a new computational tool for the phase and chemical equilibrium problem, Comput. Chem. Engrg. 21 (1) (1996) 1–23.
[4] P.J. Rabier, A. Griewank, Generic aspects of convexification with applications to thermodynamic equilibrium, Arch. Rational Mech. Anal. 118 (4) (1992) 349–397.
[5] R.T. Rockafellar, Convex Analysis, Princeton University Press, 1996.