∞ = emulsion phase
mf = minimum fluidization

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Computation of Phase and Chemical Equilibrium:

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Part I. Local and Constrained Minima in Gibbs Free Energy

Several methods are reviewed for determining compositions in multiphase, reacting mixtures at equilibrium. Wolfe's quadratic programming algorithm is applied and results compared with the Rand method (Dluzniewski and Adler 1972), NASA method (Gordon and McBride 1971) and the George et al. (1976) implementation of Powell's method. For poor guesses in compositions, local and constrained minima in Gibbs free energy may arise, giving incorrect phase distributions.

SCOPE

The objective of this research has been to devise new methods for calculating compositions in phase and chemical equilibrium that are applicable for use in simulators. The methods should provide the proper blend of generality, reliability, and speed.

Today's simulators permit calculation of phase equilibrium for, at most, three phases (vapor-liquid-liquid), involving no solids, and no chemical reaction.

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In this article, we evaluate several methods to minimize Gibbs free energy in calculating compositions in phase and chemical equilibrium. Given poor guesses for phase distribution and compositions, the global minimum in Gibbs free energy may not be computed. With too few phases, constrained minima are obtained. With the correct phase distribution, but poor guesses for compositions, the moles of species in one or more phases often approach zero. The Rand and NASA methods require removal of variables and equations to avoid singular matrices and negative moles. George et al. (1976) circumvent these steps with transformed variables. We apply the quadratic programming algorithm of Wolfe without transformed variables. This paper describes how these algorithms prevent constrained minima, but do not eliminate the possibility of convergence to a local minimum.

CONCLUSIONS AND SIGNIFICANCE

We conclude that: 1. The Rand and NASA methods, although derived differently, give nearly identical linear equations with the same coefficient matrix and, with minor exceptions, are implementations of Newton's method.

2. For these methods, when the moles of all species in a phase approach zero, a corresponding row and column of the Jacobian matrix approaches zero. To avoid singularity, the equation and mole variables are deleted from the search space. When the phase is deleted prematurely, a constrained minimum is obtained.

3. Powell's method, as implemented by George et al., avoids constrained minima, but is two-eight times slower than the Rand method for the examples tested.

4. The quadratic programming algorithm of Wolfe does not require removal of variables when moles of a phase approach zero. To reduce the search space, we eliminate these variables and find speeds for quadratic programming comparable to those for the Rand method. There is the possibility of converging to constrained minima, but we introduce a phase-splitting algorithm and test for stability of phases during minimization calculations, as described in Part II.

Figure 1 illustrates the physical situation in which a mixture of chemicals is allowed to reach equilibrium at T_f and P_f. The number of phases, P, and their compositions are unknown at equilibrium. Mathematically, the problem is to minimize the Gibbs free energy

$$G = \sum_{j=1}^{S} G_j^o n_j^c + \sum_{j=S+1}^{C} \sum_{l=1}^{P} G_{jl} n_{jl} \qquad (1)$$

subject to mass balance constraints, where C is the number of chemical species, P is the number of mixed phases (vapor, liquid, solid), S is the number of condensed species (which appear in only one pure phase, are normally solid, and do not distribute amongst other phases,) n_{jl} is the number of moles of compound j in phase l, G_{jl} is the chemical potential of compound j in phase l, given by

$$G_{jl} = G^o_{jl} + RT \ln \frac{\bar{f}_{jl}}{f^o_{jl}}$$

and, often, $\bar{f}_{jl} = y_{jl}\phi_{jl}P$ for vapor and $= x_{jl}\gamma_{jl}f_{jl}$ for liquid phases.

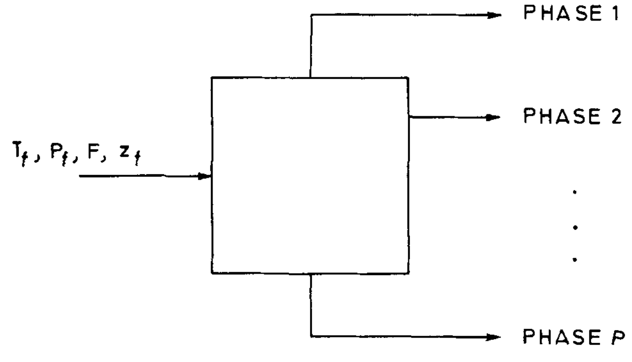

Figure 1. Physical situation: mixture reaches equilibrium at T_f and P_f. The number of phases, P, and their compositions are unknown.

When the number of independent chemical reactions equals $C - \rho$, where ρ is the rank of the atom matrix (m_{jk}), Gibbs free energy is minimized subject to atom balance constraints

$$b_k = \sum_{j=1}^{S} m_{jk} n_j^c + \sum_{j=S+1}^{C} \sum_{l=1}^{P} m_{jk} n_{jl} \quad k = 1, \ldots, E \qquad (2)$$

where b_k is the number of gram-atoms of element k, m_{jk} is the number of atoms of element k in compound j, and E is the number of elements.

PRIOR WORK

Chemical Equilibrium

Until the early 1940's, compositions in chemical equilibrium were computed manually by solving a set of nonlinear equations

$$\sum_{j=1}^{C} \nu_{ij} G_j = 0 \qquad i = 1, \ldots, R \qquad (3)$$

subject to the atom balances in Equation (2). Equation (3) was written for each of R independent reactions and was obtained by differentiating Equation (1):

$$\frac{dG}{d\xi_i} = 0 \qquad i = 1, \ldots, R$$

where ξ_i is the extent of reaction i and

$$n_j = n_j^o + \sum_{i=1}^{R} \nu_{ij} \xi_i \qquad j = 1, \ldots, C \qquad (4)$$

n_j^o is the moles of compound j in the feed mixture and ν_{ij} are the stoichiometric coefficients of compound j in reaction i given by the mass balances $\mathbf{M}^T \boldsymbol{\nu}^T = 0$.

Brinkley (1946) postulated C species present in a single phase at equilibrium. ρ species, referred to as "components," were selected to have linearly independent formula vectors, where ρ is the rank of the atom matrix, (m_{jk}), and Y_j is the formula vector for the jth species, $[m_{j1}, m_{j2}, \ldots, m_{jE}]$. Given the choice of components, the stoichiometric coefficients for an independent set of chemical reactions are computed

$$\sum_{j=1}^{\rho} \nu_{ij} Y_j = Y_i \quad i = \rho + 1, \ldots, C \tag{5}$$

where the number of independent reactions, $R = C - \rho$, and the species on the right-hand-side are referred to as "derived species." Compositions at equilibrium are calculated using Equation (3) and conservation of mass for each component

$$G_i - \sum_{j=1}^{\rho} \nu_{ij} G_j = 0 \qquad i = \rho + 1, \ldots, C \tag{6}$$

$$n_j + \sum_{i=\rho+1}^{C} \nu_{ij} n_i = q_j \qquad j = 1, \ldots, \rho \tag{7}$$

where the feed mixture is distributed amongst components, $j = 1, 2, \ldots, \rho$, and $q_j = n_j^o$. Kandiner and Brinkley (1950) assumed values for the derived species, n_i^*, and solved Equation (7) for the moles of components, n_j. Equation (6) was solved for n_i and convergence criteria checked. For convergence, components need be selected as those species present in the highest concentration at equilibrium. When this is not the case, Equation (7) frequently gives negative values for n_j.

Browne et al. (1960) suggests the "optimum component" procedure in which components are selected as those species expected to be in the highest concentration at equilibrium. Cruise (1964) altered the components during iterative calculation to reflect changes in composition. Cruise solved Equations (6) and (7) by adjusting extents of reaction. To prevent divergence, Smith and Missen (1968) also improved initial estimates by using a linear programming procedure which neglects the logarithmic terms in Equation (1).

Because of these problems, most recent methods avoid the distinction between components and derived species and take the moles of all species as iteration variables.

Naphtali (1959) solved Equation (3) by obtaining corrections to extents of reaction from

$$d\xi_i = -\Delta G_i d\lambda$$

where $d\lambda$ is the step-size and

$$\Delta G_i = \sum_{j=1}^{C} \nu_{ij} G_j$$

He showed that positive $d\lambda$ give $d\xi_i$ that reduce Gibbs free energy. This method is analogous to that of steepest descent, a first-order method for minimization of Gibbs free energy. Ma and Shipman (1972) used Naphtali's method to estimate compositions at equilibrium and the Newton-Raphson method to achieve convergence.

Phase Equilibrium

Algorithms for systems that are vapor, liquid, or a mix of vapor and liquid in equilibrium can be relatively simple. For example, the flash equation

$$\sum_{j=1}^{C} \frac{z_j(1 - k_j)}{1 + \alpha(k_j - 1)} = 0 \tag{8}$$

can be solved for α (moles of vapor/moles of feed) using simple root-finding procedures.

For non-ideal solutions, k_j is a function of liquid composition and α. Hence, Equation (8) must be solved iteratively with material balance equations and computation times increase.

For highly non-ideal solutions, involving two or less liquid phases, Henley and Rosen (1969) developed an algorithm that attempts to solve for compositions at equilibrium among a vapor and two liquid phases using k-values. When a solution cannot be obtained, attempts are made to determine compositions at equilibrium between two liquid or vapor and liquid phases.

CHEMICAL AND PHASE EQUILIBRIUM

Sanderson and Chien Method

Sanderson and Chien (1973) solve Equations (3), (4) and (8) to determine compositions of vapor and liquid phases in chemical and phase equilibrium. A set of independent chemical reactions is selected with guesses for extent of reaction. Solution of Equation (8) leads to compositions in phase equilibrium, but applies only for a vapor and liquid in equilibrium. Residuals of Equations (3) and (4) are computed and extents of reaction, ξ_i, and moles of species j, n_j^t, are adjusted using Marquardt's method (Henley and Rosen 1969).

Rand Method

In 1958, White, Johnson, and Dantzig, working at Rand Corporation, computed compositions at equilibrium using Newton's method to minimize the Gibbs free energy of an ideal gas mixture. Their algorithm was extended to include pure solid phases (Boynton 1960, Oliver et al. 1962, Balzhiser et al. 1972) and one or more mixed liquid or solid phases (Dluzniewski and Adler 1972).

In our notation, the n vector contains guessed values for the moles of compound j in phase l (n_{jl}) at equilibrium. Equation (1) is differentiated analytically (assuming $\partial\phi_{jl}/\partial n_{jl} = \partial\gamma_{jl}/\partial n_{jl} = 0$) and substituted into a quadratic Taylor Series to approximate the Gibbs free energy at the N vector, a vector of mole numbers in close proximity to the n vector

$$\begin{aligned} Q\{\mathbf{N}\} = G\{\mathbf{n}\} &+ \sum_{j=1}^{S} \frac{\partial G}{\partial n_j^c} (N_j^c - n_j^c) \\ &+ \sum_{l=1}^{P} \sum_{j=S+1}^{C} \frac{\partial G}{\partial n_{jl}} (N_{jl} - n_{jl}) \\ &+ \frac{1}{2} \sum_{j=1}^{S} \frac{\partial^2 G}{\partial n_j^{c^2}} (N_j^c - n_j^c)^2 \\ &+ \frac{1}{2} \sum_{l=1}^{P} \sum_{j=S+1}^{C} \sum_{j'=S+1}^{C} \frac{\partial^2 G}{\partial n_{jl} \partial n_{j'l}} (N_{jl} - n_{jl})(N_{j'l} - n_{j'l}) \end{aligned} \tag{9}$$

N is computed at minimum Q subject to the atom balance constraints (Equation 2). An unconstrained objective function, using Lagrange multipliers, π_k $(k = 1, 2, \ldots, E)$

$$F\{\mathbf{N}\} = Q\{\mathbf{N}\} + RT \sum_{k=1}^{E} \pi_k \left[b_k - \sum_{j=1}^{S} m_{jk} N_j^c - \sum_{l=1}^{P} \sum_{j=S+1}^{C} m_{jk} N_{jl} \right] \tag{10}$$

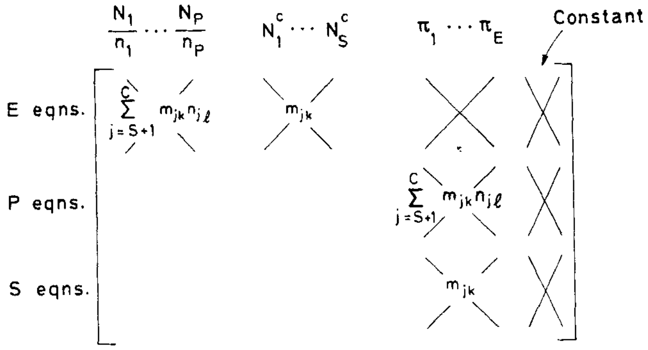

Figure 2. Coefficient matrix, Rand method (for details, see Figure 1, Part III).

is minimized using

$$\frac{\partial F\{\mathrm{N}\}}{\partial N_j{}^c} = \frac{\partial F\{\mathrm{N}\}}{\partial N_{jl}} = \frac{\partial F\{\mathrm{N}\}}{\partial \pi_k} = 0 \qquad \begin{array}{l} j = 1, \ldots, C \\ l = 1, \ldots, P \\ k = 1, \ldots, E \end{array} \tag{11}$$

Since Q is a quadratic function of N, the resulting equations are linear in unknowns $N_j{}^c$, N_{jl}, and π_k. These equations and

$$N_l = \sum_{j=1}^{C} N_{jl} \qquad l = 1, \ldots, P$$

are reduced to $S + P + E$ linear equations in unknowns $N_j{}^c$, N_l, and π_k. The coefficient matrix, shown schematically in Figure 2 (for details, including ionic species, see Figure 1, Part III), is inverted and N_{jl} are computed

$$N_{jl} = -n_{jl} \left[\frac{G_{jl}\{\mathrm{n}\}}{RT} + \frac{N_l}{n_l} + \sum_{k=1}^{E} \pi_k m_{jk} \right] \qquad l = 1, \ldots, P \tag{12}$$

Letting

$$\boldsymbol{\Delta} = \mathrm{N} - \mathrm{n} \tag{13}$$

a vector defining a search direction is obtained. New points, N′

$$\mathrm{N}' = \mathrm{n} + \lambda \boldsymbol{\Delta} \tag{14}$$

are obtained by adjusting λ to give minimum G and to avoid negative values of N_{jl} and $N_j{}^c$. We adjust λ between $\lambda_{\max}$ (maximum value of λ such that $\mathrm{N}' \geqq 0$) and $\lambda_{\min}$ (minimum value of λ such that $\mathrm{N}' \geqq 0$), with unimodality assumed. Beginning with $\lambda = \lambda_{\max}$, $dG/d\lambda$ is computed

$$\frac{dG}{d\lambda} = \sum_{j=1}^{S} \frac{G_j{}^o}{RT} \Delta_j{}^c + \sum_{j=S+1}^{C} \sum_{l=1}^{P} G_{jl} \Delta_{jl}$$

where $\partial\gamma_{jl}/\partial\lambda$ and $\partial\phi_{jl}/\partial\lambda$ are taken as zero. λ is reduced by 0.1 $\lambda_{\max}$ until a negative slope is obtained; if not found for $\lambda > 0$, a similar search is conducted for $\lambda_{\min} \leqq \lambda < 0$. When the slope turns negative in interval (0, 0.1 $\lambda_{\max}$) or (0.1 $\lambda_{\min}$, 0) a Fibonacci search reduces the interval to $\delta(\lambda_{\max} - \lambda_{\min})$. Values of $dG/d\lambda$ may be computed using γ_{jl} and ϕ_{jl} at n or N′. The former reduces computations per iteration, while the latter gives a more realistic minimum in the search direction and is used in this work.

When solid phases are incorrectly postulated to occur at equilibrium, a solution cannot be obtained. Values of $N_j{}^c$ become negative and λ becomes small (approximately zero). Oliver et al. (1962) recommend that such species be removed and the algorithm restarted. (See also Balzhiser et al. 1972). They show that the criterion for introducing a solid species is

$$\frac{G_j{}^o}{RT} - \sum_{k=1}^{E} \pi_k m_{jk} < 0 \qquad j \leqq S \tag{15}$$

where the Lagrange multipliers, π_k, are computed at minimum Gibbs free energy without the solid species. Such a check should be made, especially after a solid species has been removed.

It is often desirable to compute the compositions of trace species in solution phases, which were not included in the minimization calculations. These are given by

$$n_{jl} \simeq n_l \, e^{\left[-\frac{G_j{}^o}{RT} + \ln \beta_{jl} + \sum_{k=1}^{E} \pi_k m_{jk} \right]} \tag{16}$$

where, for a liquid

$$\beta_{jl} = \frac{\gamma_{jl} f_{jl}}{f^o{}_{jl}}$$

and γ_{jl} are at infinite dilution.

Dluzniewski and Adler (1972) used the Rand method for calculation of phase equilibrium. "Fictitious elements" are introduced to prevent reaction. Consider a reactor that produces ethylbenzene by reaction of benzene and ethylchloride in the presence of $AlCl_3$ catalyst. For calculation of phase equilibrium, downstream of the reactor, fictitious element A replaces a hydrogen atom in benzene (C_6H_5A) and the moles of each species remain unchanged.

When a mixed phase l is postulated that does not exist at equilibrium, the Rand method decreases its concentrations to zero. This causes the row and column associated with extraneous phase l in the coefficient matrix to approach zero and singularities to develop (see Figure 2). Hence, we found it necessary to remove these rows and columns from the matrix during matrix inversion when the maximum pivot element is less than an arbitrarily small value.

NASA Method

Gordon and McBride (1971), working at the NASA Lewis Research Center, developed an algorithm similar to the Rand method. They minimized

$$F\{\mathrm{n}\} = G\{\mathrm{n}\} + RT \sum_{k=1}^{E} \pi_k \left(b_k - \sum_{j=1}^{S} m_{jk} n_j{}^c - \sum_{j=S+1}^{C} m_{jk} n_j \right) \tag{17}$$

$$\frac{\partial F\{\mathrm{n}\}}{\partial n_j{}^c} = \frac{\partial F\{\mathrm{n}\}}{\partial n_j} = \frac{\partial F\{\mathrm{n}\}}{\partial \pi_k} = 0 \tag{18}$$

The resulting $C + E$ equations are nonlinear in unknowns $n_j{}^c$, n_j, and π_k; but ln n_j are iteration variables since n_j occur in logarithm terms. These equations are linearized using first-order Taylor Series (Newton-Raphson method), in the variables $\Delta n_j{}^c$, $\Delta(\ln n_j)$, and π_k, and with $n = \sum_j n_j$ are reduced to $S + 1 + E$ linear equations in unknowns $\Delta N_j{}^c$, $\Delta(\ln N)$, and π_k. We have shown that they are nearly identical to the equations in the Rand method and have the same coefficient matrix (Figure 2).

Implementation of Powell's Method

George et al. (1976) eliminate constraints, $n_j \geqq 0$, by introducing an allocation function

$$A\{u_j\} = \frac{1}{1 + e^{-u_j}} \tag{19}$$

where $-\infty < u_j < \infty$ and $0 \leqq A\{u_j\} \leqq 1$. For two phases in equilibrium, without reaction,

$$\left.\begin{aligned} n_{j1} &= A\{u_j\}n_j^t \\ n_{j2} &= (1 - A\{u_j\})n_j^t \end{aligned}\right\} \quad j = 1, \ldots, C \tag{20}$$

and for three phases, without reaction

$$\begin{aligned} n_{j1} &= A\{u_j\}n_j^t \\ n_{j2} &= (1 - A\{u_j\})A\{u_{j+C}\}n_j^t \\ n_{j3} &= (1 - A\{u_j\})(1 - A\{u_{j+C}\})n_j^t \\ & \qquad\qquad j = 1, \ldots, C \end{aligned} \tag{21}$$

where $n_j^t = \sum_{l=1}^{P} n_{jl} = n_j^o$. In calculations to minimize G, u_j replace n_{jl} as iteration variables; there are $(P - 1)C$ elements in $\mathbf{u}$.

For systems with reaction, George et al. (1976), like Brinkley (1946), select ρ "components" and $C - \rho$ "derived species." For the derived species, $C - \rho$ additional elements, u_j, are defined such that

$$n_j^t = A\{u_{j+(P-1)C}\}n_{j\max} \quad j = \rho + 1, \ldots, C \tag{22}$$

and

$$n_{j\max} = \frac{1}{\underset{k=1,\ldots,E}{\max}\left[\dfrac{m_{jk}}{b_k}\right]}$$

where $n_{j\max}$ is the maximum amount of species j at equilibrium. These elements, u_j, are also adjusted to minimize G. As recognized by Kandiner and Brinkley (1950), care must be taken to select "components" from among those species present in highest concentration at equilibrium. Otherwise, during calculations to minimize G, large values of n_j^t for the derived species ($j = \rho + 1, \ldots, C$) can give negative values of n_j^t for trace components when solving Equation (7).

George et al. (1976) implemented Powell's method (1970), a quasi-Newton method, that uses approximations to the Hessian matrix and its inverse, $\tilde{H}\{\mathbf{u}\}$ and $\tilde{H}\{\mathbf{u}\}^{-1}$, to calculate $\boldsymbol{\Delta}$ $(= \mathbf{N} - \mathbf{n})$.

Chemical Equilibrium with Isomers

For mixtures containing isomers, the number of independent chemical reactions R is often not given by $C - \rho$, where ρ is the rank of the atom matrix. Whitwell and Dartt (1973) describe methods for determining R and mass balance constraints for minimization of Gibbs free energy.

Restricted Chemical Equilibrium

For some mixtures, experimental measurements show that fewer than $C - \rho$ reactions describe the mixtures at equilibrium. This occurs when some of $C - \rho$ reactions do not occur due to the formation and depletion of free radicals in the reaction mechanism (Bjornbom 1975, 1977) or because "certain reaction paths are not available for chemical change" (Prigogine and Defay 1947). The latter occurs for certain reactions, in the absence of catalyst, that are too slow to occur.

For these systems, mass balances must account for these restrictions and replace the atom balances (2) as constraints for minimization of Gibbs free energy. These mass balances were determined by Schott (1964)

$$q'_j = \sum_{j=1}^{S} m'_{jj'}n_j^c + \sum_{j=S+1}^{C}\sum_{l=1}^{P} m'_{jj'}n_{jl} \quad j' = 1, \ldots, \rho' \tag{23}$$

where $\rho' = C - R$ and R is the number of reactions observed experimentally. Schott solved for unknown coefficients in the $\mathbf{M}'$ matrix, where

$$\mathbf{M}'\boldsymbol{\nu}^T = 0 \tag{24}$$

$\mathbf{M}'$ is a $C \times \rho'$ matrix given by $[\mathbf{I} \mid \mathbf{X}]^T$ and $\mathbf{X}$ is a submatrix of unknown coefficients. Bjornbom (1975) shows that extents of R independent reactions must vary independently.

QUADRATIC PROGRAMMING

Quadratic programming algorithms are attractive for calculating compositions in phase and chemical equilibrium, because they satisfy inequality constraints ($\mathbf{N} \geqq 0$) without transformations. Moles of solid species approach zero, rather than large negative values, when solid species are removed during minimization calculations. Hence, their variables can be retained during subsequent calculations. Similarly, for solution phases, when the moles of all species approach zero, variables may be retained. For these reasons, we implemented the quadratic programming algorithm of Wolfe (Hadley 1964 and Kunzi et al. 1966) and compared its performance to that of the Rand method and the George et al. (1976) implementation of Powell's method.

Quadratic programming algorithms use the Kuhn-Tucker conditions (Kunzi et al. 1966) to minimize quadratic objective functions (Equation 9) subject to equality constraints, e.g., Equation (2) or appropriate mass balances, and inequality constraints ($\mathbf{N} \geqq 0$). For minimization of the quadratic approximation to Gibbs free energy, these reduce to

$$\begin{gathered} 2\mathbf{CN} - \mathbf{V} + \mathbf{M}\boldsymbol{\pi} = -\mathbf{p} \\ \mathbf{MTN} = \mathbf{b} \\ \mathbf{N^TV} = 0 \\ \mathbf{N} \geqq 0, \quad \mathbf{V} \geqq 0 \end{gathered} \tag{25}$$

where $\mathbf{C} = \frac{1}{2}\,\nabla^2\mathbf{G}\{\mathbf{n}\}$, $\mathbf{p} = \nabla\mathbf{G}\{\mathbf{n}\} - \nabla^2\mathbf{G}\{\mathbf{n}\} \cdot \mathbf{n}$, $\mathbf{V} = \partial F/\partial\mathbf{N}$, and $\mathbf{M}$ is the atom matrix.

Wolfe uses the Simplex Algorithm of linear programming to solve these equations in two phases. He introduces slack variables $\mathbf{z}^1$, $\mathbf{z}^2$, and $\mathbf{w}$

$$\begin{gathered} 2\mathbf{CN} - \mathbf{V} + \mathbf{M}\boldsymbol{\pi} + \mathbf{z}^1 - \mathbf{z}^2 = -\mathbf{p} \\ \mathbf{MTN} + \mathbf{w} = \mathbf{b} \\ \mathbf{N} \geqq 0, \quad \mathbf{V} \geqq 0, \quad \mathbf{z}^1 \geqq 0, \quad \mathbf{z}^2 \geqq 0, \quad \mathbf{w} \geqq 0 \end{gathered} \tag{26}$$

Initially $\mathbf{N} = \mathbf{V} = \boldsymbol{\pi} = 0$ and

$$\begin{aligned} z_i^1 &= -p_i, \quad z_i^2 = 0 \quad \text{if} \quad p_i < 0 \\ z_i^1 &= 0, \qquad z_i^2 = p_i \quad \text{if} \quad p_i > 0 \\ \mathbf{w} &= \mathbf{b} \end{aligned}$$

In Phase 1, the Simplex Algorithm is used to minimize

$$\sum_{k=1}^{E} w_k \tag{27}$$

Table 1. Execution Times for the Rand Method, Quadratic Programming (Wolfe's Algorithm), and the Implementation of Powell's Method by George et al. Programs are in Fortran and Execution Times are for the Univac 90/70 Computer

	Execution time, sec*		
	Rand	Quad. prog.	George et al.
1. Ideal gas with reaction	2	3	4
2. Reacting gas with solid phase	2	3	
3. Two liquid phases, no reaction	2	4	7
4. Vapor and liquid phases, no reaction	18	18	101
5. Three liquid phases, no reaction	4	6	11
6. Vapor and two liquid phases, no reaction	5	7	41
7. Vapor and liquid phases, reaction	2	3	20

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* Convergence criteria: $||\nabla G|| \leq \delta = 10^{-4}$.

subject to Equations (26) and $\mathbf{V} = \boldsymbol{\pi} = 0$. $\mathbf{w}$ is eliminated from the basis ($w_k \rightarrow 0$) and replaced by $\mathbf{N}$. In Phase 2,

$$\sum_{i=1}^{S+PC} z_i^1 + z_i^2 \tag{28}$$

is minimized subject to Equations (26) only. The z^1 and z^2 are eliminated from the basis and replaced by $\mathbf{V}$ and $\boldsymbol{\pi}$. To satisfy $\mathbf{N}^T\mathbf{V} = 0$, if N_i is in the basis, V_i cannot enter the basis, and vice versa. When $\mathbf{C}$ is positive semidefinite, this condition keeps $\mathbf{z}^1$ and $\mathbf{z}^2$ from being eliminated entirely. A small positive number is added to the diagonal elements of $\mathbf{C}$ to create a positive definite matrix and Phase 2 is completed (see Charnes Perturbation Method, Charnes and Cooper 1961).

If convergence criteria are not satisfied, $\mathbf{n} \leftarrow \mathbf{N}$, and Equations (25) are resolved. When all values of N_{jl}, $j = 1, \ldots, C$ are zero, these variables for phase l are eliminated from Equations (25), to avoid unnecessary operations. However, upon examining the solution, care must be taken to ascertain that the phase does not exist at equilibrium. In our work, this is accomplished by the phase-splitting algorithm introduced in Part II. Alternatively, the variables N_{jl} for phase l can be retained with zeroes and the quadratic programming algorithm may adjust them greater than zero. When phase l exists at equilibrium, but N_{jl} remain zero, a local minimum is achieved. The next section clarifies this point.

Computed results were obtained for the following systems, using quadratic programming, the Rand method, and the George et al. implementation of Powell's method:

1. *Ideal gas with reaction.* Ethane cracking at 1,000 K and 1.013 bar (1 atm) (Balzhiser et al. 1972).

2. *Reacting gas with solid phase.* Blast furnace equilibrium at 1,367 K (2,000°F) and 1.013 bar (1 atm) (Balzhiser et al. 1972).

3. *Two liquid phases with no reaction.* Mixture of isopropyl alcohol, isopropyl ether and water at 335 K and 1.013 bar (1 atm) (Dluzniewski and Adler 1972).

4. *Vapor and liquid phases with no reaction.* Mixture of isopropyl alcohol, isopropyl ether, propylene, n-propanol, water, acetone, and hexene at 388.7 K (240°F) and 41.36 bar (600 psia) (Dluzniewski and Adler 1972).

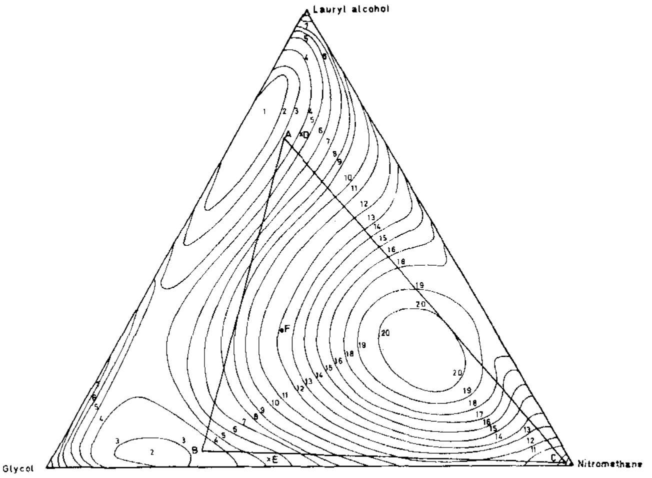

Figure 3. Contours of constant Gibbs free energy of mixing for mixture of glycol, lauryl alcohol, and nitromethane at 295.2K and 1.013 bar (1 atm). Activity coefficients using van Laar equation.

5. *Three liquid phases with no reaction.* Mixture of lauryl alcohol, glycol, and nitromethane at 295.2 K and 1.013 bar (1 atm) (Null 1970).

6. *Vapor and two liquid phases with no reaction.* Mixture of propylene, water, isopropyl ether and isopropyl alcohol at 378 K and 41.33 bar (40.8 atm) (Dluzniewski and Adler 1972).

7. *Vapor and liquid phases with reaction.* Reaction of ethanol and acetic acid to give ethyl acetate and water at 358.2 K and 1.013 bar (1 atm) (Sanderson and Chien 1973).

Table 1 shows the number of iterations and execution time for the three methods. Quadratic programming and the Rand method have comparable speeds, whereas the implementation of Powell's method by George et al. (1976) is two to eight times slower. This is expected as experiments to minimize the Rosenbrock function show Powell's method to be slower than Newton's method, using analytical and numerical derivatives. Powell's method typically requires five times fewer function evaluations than Newton's method using numerical derivatives; but, much computation time is consumed in updating $\bar{H}\{\mathbf{u}\}$ and $\bar{H}\{\mathbf{u}\}^{-1}$.

Analytical derivatives (assuming $\partial\phi_{jl}/\partial n_{jl} = \partial\gamma_{jl}/\partial n_{jl} = 0$) are used for the Rand method and quadratic programming; numerical derivatives for the method of George et al. In all cases, the correct number of phases (at equilibrium) were assumed.

LOCAL AND CONSTRAINED MINIMA

Equilibrium compositions are given at the global minimum of the Gibbs free energy surface. But, poor guesses for phase distribution and composition can lead to local or constrained minima. A local minimum occurs when the minimization algorithm converges to a minimum point with $N_{jl} = 0$, $j = 1, \ldots, C$, where phase l is present at equilibrium. A constrained minimum point is obtained when the variables N_{jl} are eliminated from the search space prematurely, as they first approach zero. Constrained minima occur when too few phases are assumed. Local or constrained minima occur when the correct number of phases are assumed, but composition guesses are poor, and can occur when too many phases are assumed. In the latter case, as extraneous phases are re-

Table 2. Phase Equilibrium for a Mixture of 40% Glycol, 30% Lauryl Alcohol, and 30% Nitromethane, at 295.2 K and 1.013 Bar (1 atm). Activity Coefficients Using van Laar Equation. Interaction Coefficients Given by Null (1970), N_{jl} are Tabulated

	Total moles	Guesses			Equilibrium		
		Phase 1	Phase 2	Phase 3	Phase 1	Phase 2	Phase 3
Glycol	0.4	0.1	0.295	0.005	0.0723	0.3262	0.0014
Lauryl alcohol	0.3	0.25	0.04	0.01	0.2825	0.0163	0.0012
Nitromethane	0.3	0.05	0.05	0.2	0.0375	0.1283	0.1341

moved, if composition guesses are poor, local or constrained minima can be reached.

For mixtures of glycol, lauryl alcohol, and nitromethane (Null 1970), a contour plot of Gibbs free energy of mixing is shown in Figure 3, computed using

$$\Delta G_m = G - \sum_{j=1}^{3} n_j^t G_j^o = RT \sum_{j=1}^{3} n_j^t \ln \gamma_j x_j^t \qquad (29)$$

and the van Laar equation for liquid activity coefficients. Along the borders, for glycol-nitromethane and lauryl alcohol-nitromethane, two minima are observed, illustrating the partial miscibility of these binary pairs. The glycol-lauryl alcohol pair is also partially miscible, but two minima are not observed—probably due to limitations of the van Laar model. Since a tangent plane passes through three points in the Gibbs free energy surface (A, B, and C), the van Laar model shows three phases in equilibrium for mixtures within triangle ABC. Substituting these compositions (see Table 2) in Equation (1), the global minimum of the Gibbs free energy surface is obtained (*not* the minimum of Equation 29), $G_{\min}/RT = -3.5617$.

When too few phases are assumed, the search for minimum Gibbs free energy is conducted along a boundary of the feasible search space. Figure 4 is an attempt to show this phenomenum in three dimensions. Gibbs free energy is plotted as a function of the moles of component 1 in phases L_1 and L_2. If $n_1^{L_2}$ is not in the search space, the search for minimum Gibbs free energy is constrained to the boundary, along the curve *RST* and a constrained minimum at *T* is found.

To illustrate this result, consider minimization of Gibbs free energy for a mixture of 40% glycol, 30% lauryl alcohol, and 30% nitromethane (Point F—Figure 3), assuming that two phases exist at equilibrium. One solution contains two phases, Points D and E in Figure 3, with compositions tabulated in Table 3, and $G_{\min}/RT = -3.535$. Even when three phases are assumed to exist at equilibrium, with poor guesses for composition (see Table 4), the variables N_{j3} are removed during minimization using the Rand method and a constrained minimum is found. In our implementation of quadratic programming, the variables N_{j3} were eliminated, as well. We developed the phase-splitting algorithm described in Part II to explore the feasibility of this phase reappearing after subsequent iterations. We reduce the size of the search-space, thereby saving considerable computation time, but add computations in phase-splitting. This trade-off and reliability are considered in Part II.

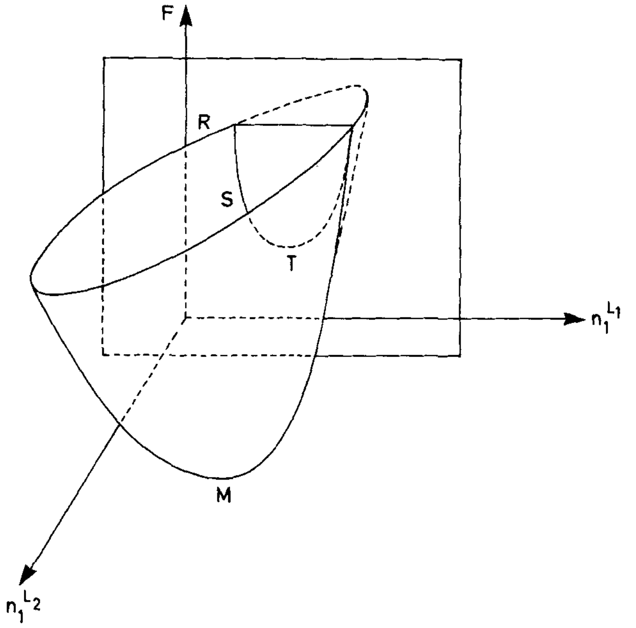

Figure 4. Hypothetical surface of Gibbs free energy shows $G\{n_1^{L_1}, n_1^{L_2}\}$. Additional axes cannot be shown for $n_j^{L_1}$ and $n_j^{L_2}$ in multicomponent mixtures.

Table 3. Minimum Point of Gibbs Free Energy for a Mixture of 40% Glycol, 30% Lauryl Alcohol, and 30% Nitromethane, at 295.2 K and at 1.013 Bar (1 atm), Assuming Two or Less Phases

	Total moles	Composition at $G_{\min}$		
		Phase 1	Phase 2	Phase 3
Glycol	0.4	0.0585	0.3415	—
Lauryl alcohol	0.3	0.2845	0.0155	—
Nitromethane	0.3	0.0466	0.2533	—

Table 4. Minimum Point of Gibbs Free Energy for a Mixture of 40% Glycol, 30% Lauryl Alcohol, and 30% Nitromethane, at 295.2 K and 1.013 Bar (1 atm), Assuming Three Phases with Poor Guesses for Composition

	Total moles	Guesses			Composition at $G_{\min}$		
		Phase 1	Phase 2	Phase 3	Phase 1	Phase 2	Phase 3
Glycol	0.4	0.045	0.295	0.06	0.0585	0.3415	—
Lauryl alcohol	0.3	0.25	0.04	0.01	0.2845	0.0155	—
Nitromethane	0.3	0.24	0.05	0.01	0.0466	0.2533	—

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NOTATION

A = allocation function
b_k = gram atoms of element k
C = number of chemical species
$\mathbf{C}$ = $1/2\ \nabla^2\mathbf{G}\{\mathbf{n}\}$
E = number of elements
f_{jl} = fugacity of pure compound j in phase l at T and and P of system
$\bar{f}_{jl}$ = mixture fugacity of compound j in phase l at T and P of system
f^o_{jl} = fugacity of compound j in standard state for phase l
F = unconstrained objective function (see Equation 10)
G = Gibbs free energy
G^o_{jl} = free energy of formation of species j in standard state for phase l
G_{jl} = partial molal free energy of compound j in phase l (chemical potential)
ΔG_m = Gibbs free energy of mixing
$\mathcal{H}$ = approximation to Hessian matrix
$\mathcal{H}^{-1}$ = approximation to inverse of Hessian matrix
k_j = vapor-liquid equilibrium constant for compound j
m_{jk} = number of atoms of element k in compound j
$\mathbf{M}$ = atom matrix-elements are m_{jk}
$\mathbf{M}'$ = mass balance matrix
n_{jl} = moles of compound j in phase l
n_j^c = moles of condensed species j
n_j^o = moles of compound j in feed mixture
n_j^t = moles of compound j at equilibrium
$n_{j\max}$ = maximum moles of species j at equilibrium
$\mathbf{n}$ = guess vector for moles of compound j in phase l
$\mathbf{N}$ = vector of moles of compound j in phase l computed using Equation (10)
$\mathbf{p}$ = $\nabla\mathbf{G}\{\mathbf{n}\} - \nabla^2\mathbf{G}\{\mathbf{n}\}\cdot\mathbf{n}$
P = number of mixed phases (vapor, liquid, or solid); pressure
q_j = equals n_j^o, where feed mixture is distributed amongst ρ "components"
q_j' = equals n_j^o, where feed mixture is distributed amongst ρ' "components"
Q = quadratic approximation of Gibbs free energy surface
R = number of independent reactions, universal gas constant
S = number of condensed species, appear in only one pure phase, normally solid, do not distribute among other phases
T = absolute temperature
$\mathbf{u}$ = vector of transformed variables
$\mathbf{U}$ = new vector of transformed variables
$\mathbf{V}$ = $\partial F/\partial \mathbf{N}$
$\mathbf{w}$ = vector of slack variables
x_{jl} = mole fraction of species j in phase l
x_j^t = $n_j^t \Big/ \sum_{j=S+1}^{C} n_j^t$
$\mathbf{X}$ = submatrix of $\mathbf{M}'$
y_{jl} = mole fraction of species j in vapor phase l
$\mathbf{Y}_j$ = formula vector for compound j $[m_{j1}, m_{j2}, \ldots, m_{jE}]$
z_j = mole fraction of compound j in feed
$\mathbf{z}^1$ = vector of slack variables
$\mathbf{z}^2$ = vector of slack variables

Greek Symbols

α = moles of vapor per mole of feed
β_{jl} = often $\gamma_{jl}f_{jl}/f^o_{jl}$ for liquid and $\phi_{jl}P/f^o_{jl}$ for vapor
γ_{jl} = activity coefficient of compound j in phase l
$\boldsymbol{\Delta}$ = vector defining search direction
δ = convergence tolerance
λ = parameter in unidirectional search
$d\lambda$ = step-size in Naphtali method
ν_{ij} = stoichiometric coefficient of compound j in reaction i
$\boldsymbol{\nu}$ = stoichiometric coefficient matrix
ϕ_{jl} = fugacity coefficient of compound j in phase l
π_k = Lagrange multipliers
$\boldsymbol{\pi}$ = vector of Lagrange multipliers
ρ = rank of atom matrix (m_{jk})
ξ_i = extent of reaction i

Subscript

f = feed

Superscript

c = condensed phase (comprised of a pure species that occurs in condensed phase only)

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Part II. Phase-splitting

A phase-splitting algorithm is coupled with the Rand method to improve its efficiency and reliability when the phase distribution is unknown at equilibrium. The coupled algorithm works well to give phase-splits in the metastable region where most stability tests fail. Exhaustive tests show fine performance in the region near liquid-liquid phase envelopes for systems with at least one partially miscible binary pair.

SCOPE

In Part I, we show that algorithms to calculate compositions in phase and chemical equilibrium can converge to local or constrained minima in Gibbs free energy. This paper is intended to present strategies that are more efficient and reliable for finding the global minimum.

One strategy is to assume the maximum number of phases given by the Gibbs Phase Rule:

$$P_{max} = C - R - f + 2$$

where $f = 2$, given specifications for temperature and pressure. Minimization algorithms, such as the Rand method and quadratic programming, eliminate extraneous phases, but may eliminate one or more phases improperly, given poor composition guesses. Further, these algorithms search the largest composition space and require large computation times.

The probability of reaching local or constrained minima increases with non-ideality and uncertainty in guessed compositions. This occurs particularly when processes involving non-ideal mixtures, with or without reaction, are analyzed using iterative procedures that produce large temperature and extent of reaction changes, increasing uncertainties in guessed compositions. Typical processes are:

1. **Heterogeneous distillation towers, where two liquid phases may occur on one or more trays,**
2. **Methanation reactors, where carbon may or may not deposit on Ni catalyst,**
3. **Cryogenic separators, where CO_2 may or may not freeze out, and**
4. **Extraction trains, where one, two, or three liquid phases may occur in one or more units.**

An alternative minimization strategy is to guess too few phases and to test for instability of phases during equilibrium calculations. Boston and Fournier (1978) illustrate this approach for splitting a nonideal liquid phase into two liquid phases. They use k-value algorithms to converge equilibrium calculations after splitting the liquid phase.

In this paper we introduce algorithms to split both vapor and liquid phases. Our algorithm permits very poor guesses for phase distribution; for example, all vapor or all liquid. Vapor or liquid phases are added as necessary during calculations to minimize Gibbs free energy. The search space is small and the phase-splitting algorithm has been successful in avoiding local and constrained minima for the systems tested.

CONCLUSIONS AND SIGNIFICANCE

The phase-splitting algorithm in this paper and the Rand algorithm (Newton's method) for minimization of Gibbs free energy have been tested for many systems. It is concluded that:

1. The phase-splitting algorithm improves the efficiency and reliability of the Rand algorithm (or any other minimization algorithm). Without the phase-splitting algorithm, random guesses for phase distribution led to no solution in 39 of 50 cases. With phase-splitting and very poor guesses (single liquid or vapor phase), the global

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