Partial Molar Excess Properties, Null Spaces, and a New Update for the Hybrid Method of Chemical Process Design

A new thermodynamically consistent quasi-Newton formula is proposed for building iterative representations of the approximated part of the Jacobian matrix in the hybrid method of chemical process design. This update exploits the fact that the excess enthalpy and activity coefficient functions are homogeneous functions of degree zero in mole numbers which, in turn, gives rise to a natural null space for the approximated part of the Jacobian matrix that is defined by the component molal flow rates. The new formula builds iterative approximated parts that satisfy this null space constraint in addition to the usual overall secant condition and the desired sparsity constraints.

The new quasi-Newton formula is derived using the variational calculus approach first for the nonsparse case. This solution is then extended to the sparse case.

The new updating formula, which is applicable to any chemical process design problem that involves nonideal phase equilibria and/or enthalpy of mixing considerations, is compared to the modified Schubert update in the context of the hybrid method. It is also compared to an implementation of Newton's method in which the approximated part of the Jacobian matrix is calculated by finite differences. Using an adiabatic single stage flash problem for a binary mixture with strongly nonideal liquid phase behavior, it is shown that the new updating formula compares favorably with finite differencing and can result in solutions to problems for which the original hybrid method fails.

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The hybrid method of chemical process design is a Newton-based fixed-point method that makes combined use of analytical derivative information and a modification of the quasi-Newton update of Schubert.

When applied to chemical processes whose model includes nonideal thermodynamics and when viewed in terms of both reliability and computational efficiency, the numerical results obtained thus far in support of the hybrid method have been quite positive. In particular, for many problems the hybrid method exhibits the reliability of Newton's method but at a significant reduction in computational cost, since it avoids finite differencing. Moreover, the results show that the hybrid method is both more robust and more efficient than Schubert's method.

While the numerical performance of the hybrid method has been positive, there are chemical process design problems for which Newton's method succeeds in finding the solution but for which the original hybrid method either performs very poorly or fails. This unwanted behavior is often due to thermodynamically inconsistent approximations to the matrix of derivatives of nonideal thermodynamic quantities, which are built by the modified Schubert update.

This work proposes a new thermodynamically consistent updating formula to be used in the context of the hybrid method. This new quasi-Newton update exploits the additional property of the zero-degree homogeneity of the nonideal thermodynamic functions usually involved in chemical process design calculations, the excess enthalpy and activity coefficient functions. A derivation of the new formula using variational calculus is also included.

A small set of example problems involving a binary mixture with strongly nonideal liquid phase behavior is presented to compare the new updating formula to finite differencing and the modified Schubert update.

CONCLUSIONS AND SIGNIFICANCE

A new thermodynamically consistent updating formula was suggested for use in the hybrid method of chemical process design. This new quasi-Newton update was derived using variational calculus by making use of the fact that the excess enthalpy and activity coefficients are homogeneous functions of degree zero.

The new update was compared to finite differencing and the modified Schubert update. Besides bringing the theoretical properties of the hybrid method closer to those of Newton's method, at least for design problems involving nonideal thermodynamics, preliminary numerical tests show that this new updating formula can also result in better numerical performance than the modified Schubert update. In particular, it can solve design problems for which the original hybrid method fails.

INTRODUCTION

In recent years interest in the equation-oriented approach to chemical process design has grown substantially. It is well-known that the reason for this is largely due to the inherent computational difficulties associated with the more traditional sequential modular approach to design. That is, for design problems involving recycle streams and/or design specifications, the modular approach necessarily requires nested iteration and this can result in large computational overheads and/or convergence difficulties. In contrast, the equation-oriented approach solves all of the model equations for the process simultaneously and thus involves only one level of iteration.

The algorithms that have been most successful in equation-oriented chemical process design applications are the class of methods known as Newton-based fixed-point methods. This class includes Newton's method, the nonsymmetric quasi-Newton methods of Broyden (1965, 1971) and Schubert (1970), and the hybrid method which was recently suggested for use in process design by Lucia and Macchietto (1983).

When used to solve multicomponent separation problems with nonideal phase equilibria, the overall behavior of these algorithms can be characterized as follows. Newton's method is very robust (i.e., fails least often) but can often be expensive. This expense is due to the fact that many K-value and enthalpy calculations are necessary to secure certain required physical properties derivatives when a complex expression is used for the excess Gibbs free energy. That is, for a sufficiently complex model for the excess Gibbs free energy function, the composition and temperature derivatives of activity coefficients and excess enthalpies, which are often necessary for convergence, must usually be computed by finite differences. Thus, because the physical properties calculations usually dominate the time required for the solution of these problems, finite differencing, and therefore Newton's method, can be expensive.

In contrast, quasi-Newton methods like the Broyden or Schubert update do not require expensive finite-difference calculations because they estimate partial derivatives from secant information that is gathered iteratively. Therefore, it might appear that these quasi-Newton methods offer some improvement in efficiency. However, they generally do not. More specifically, the Broyden and Schubert methods frequently require many more iterations than Newton's method, which offsets any advantage in computational efficiency per iteration that they may have. In fact, for many problems Newton's method is superior even when the total number of rigorous physical properties calculations is used to measure efficiency. Moreover, the quasi-Newton methods do not exhibit nearly as great a reliability as Newton's method on separation problems. This poor performance of quasi-Newton methods on multicomponent separation problems is, in our opinion, due to the fact that such problems can exhibit a poor natural variable scaling, and the fact that the Broyden and Schubert updates are not invariant under affine transformations of the variables.

Finally, in a recent paper Lucia and Macchietto (1983) have suggested the use of a hybrid method for equation-oriented chemical process design. When applied to separation problems, this hybrid method makes use of analytical partial derivative information for much of the Jacobian matrix since it is readily available, and uses the Schubert update to approximate any nonideal thermodynamic derivatives such as activity coefficient and excess enthalpy-composition derivatives. Lucia and Westman (1984) and Westman et al. (1984) have shown that this hybrid algorithm can be both an efficient and reliable method for solving multicomponent separation problems. That is, for the problems studied in those papers, as well as for many others, the hybrid method has demonstrated the reliability of Newton's method. However, for many problems it is considerably more efficient than Newton's method, frequently using between 50 and 70% fewer rigorous physical properties calculations. Moreover, Westman et al. have shown that the hybrid method is both more robust and more efficient than the Schubert update. Finally, Miller and Lucia (1983) have demonstrated that the hybrid method, like the Broyden and Schubert updates, can be adversely affected by variable scaling and have presented an implementation that minimizes these bad effects. Quantitative support for the performance characterizations of Newton's method, the fixed scale quasi-Newton methods, and the hybrid method can be found in the papers by Lucia and coworkers.

While the numerical performance of the hybrid method has been overwhelmingly positive, we have found multicomponent separation problems for which Newton's method is successful but for which the hybrid method fails. Moreover, after taking a closer look at these problems, we discovered something that we perhaps should have recognized long ago. The hybrid method, when used to solve multicomponent separation problems, uses the Schubert update to approximate the matrix of terms involving the derivatives of nonideal thermodynamic quantities such as activity coefficient and excess enthalpy-composition and temperature derivatives. For problems formulated in terms of component flow rates, this matrix, which is called the approximated part of the Jacobian matrix, contains elements that are either a function of a partial molar excess property or related to a partial molar excess property. For example, the partial derivatives of any equilibrium equation with respect to liquid component flow rates involve terms that contain the derivatives of the natural log of the activity coefficient, which are of course related to the partial molar excess Gibbs free energy. Similarly, derivatives of the energy balance involve derivatives of the excess enthalpy function and these are also contained in the approximated part.

It is well-known that such functions (i.e., the excess Gibbs free energy and the excess enthalpy) are homogeneous functions and, in particular, the functions whose derivatives are contained in the approximated part are homogeneous functions of degree zero in mole numbers. This in turn means that the approximated part of the Jacobian matrix has a natural null space defined by the liquid component molar flow rates. It contains a nontrivial singularity. Furthermore, it is important to note here that a finite-difference representation of the approximated part will necessarily possess this natural null space at each iteration of the calculations. However, if the Schubert update is used to build the approximated part, such approximations will not usually have the correct null space.

In this paper we derive a new update for the hybrid method of chemical process design that ensures that the sequence of approximated parts not only satisfies the usual secant condition but also has the correct null space at each iteration of the calculations. Accordingly, the remainder of the report is organized in the following way. First, we present a simple illustrative example in order to make the ideas related to homogeneous functions already presented both clearer and more formal. In particular, we show that the zero-degree homogeneity of the activity coefficients and excess enthalpy give rise to a natural null space (or kernel) and that this kernel is defined by the component flow rates. Next, we derive a new quasi-Newton update to be used in the context of the hybrid method that exploits this homogeneity. That is, we derive a new update that builds approximated parts of the Jacobian matrix that have the correct null space in addition to satisfying the usual secant and sparsity conditions. We also give an algorithm for its implementation. Finally, we present some numerical results that show that this new thermodynamically consistent update, again in the context of the hybrid method, can solve problems for which the original hybrid method fails.

AN ILLUSTRATIVE EXAMPLE

In order to make the idea of homogeneity that we wish to exploit both clearer and more formal, consider the simple example of flashing a multicomponent mixture in a single flash drum at a specified pressure and with a fixed heat duty. The equations that model this process are given by the component mass balances

$$f_i - \ell_i - v_i = 0, \quad i = 1,2,\ldots,n_c \tag{1}$$

the equilibrium equations

$$K_i \ell_i \Big/ \left(\sum_{j=1}^{n_c} \ell_j\right) - v_i \Big/ \left(\sum_{j=1}^{n_c} v_j\right) = 0, \quad i = 1,2,\ldots,n_c \qquad (2)$$

and the energy balance equation

$$H_f \sum_{i=1}^{n_c} f_i - H \sum_{i=1}^{n_c} \ell_i - h \sum_{i=1}^{n_c} v_i + Q = 0, \qquad (3)$$

where f_i, ℓ_i and v_i are the feed, liquid, and vapor ith component molal flow rates respectively; K_i is an equilibrium ratio or K-value; H_f, H, and h denote the enthalpy of the feed, liquid product, and vapor product, respectively; and Q is the flash drum heat duty. Finally, i is used to denote the component index, and n_c is the total number of components in the mixture.

As stated earlier, all equation-oriented procedures for solving the foregoing model equations of which we are aware fall under the heading of Newton-based fixed-point methods. This includes Newton's method, the Broyden and Schubert updates, and the hybrid method, as well as others. In order to put these methods within a common framework, it is convenient to let x denote the vector of unknown variables (in this case, the ℓ_i's, the v_i's, and the temperature T for the flash drum). Also, f is the collection of model equations and $J(x)$ denotes the Jacobian matrix of f. Moreover, we suppose that $J(x)$ can be written as

$$J(x) = C(x) + A(x), \qquad (4)$$

where $C(x)$, which is called the computed part of the Jacobian matrix, represents any partial derivative information that is readily available in analytical form and $A(x)$, the approximated part, contains any terms involving derivative information that is difficult and/or expensive to obtain. In general, for separation problems $A(x)$ will usually contain terms involving the derivatives of nonideal thermodynamic quantities like activity coefficient and excess enthalpy-composition and temperature derivatives. More specifically, for the illustrative example if the variables are ordered as ℓ_i's, v_i's and T and the equations are ordered as they appear (i.e., 1 through 3), then the corresponding computed and approximated parts of the Jacobian matrix, assuming that the fugacity coefficients and vapor enthalpy mixing term are functions of temperature only, are given by

$$C(x) = \begin{bmatrix} -1 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ \vdots & & \vdots & \vdots \\ 0 & & -1 & 0 \\ \dfrac{[(\Sigma_j \ell_j)K_1 - K_1\ell_1]}{(\Sigma_j \ell_j)^2} & \dfrac{-K_1\ell_1}{(\Sigma_j \ell_j)^2}\cdots & \dfrac{-K_1\ell_1}{(\Sigma_j \ell_j)^2} & \dfrac{[-\Sigma_j v_j + v_1]}{(\Sigma v_j)^2} \\ \vdots & & \vdots & \vdots \\ \dfrac{-K_{n_c}\ell_{n_c}}{(\Sigma_j \ell_j)^2}\cdots & & \dfrac{[(\Sigma_j \ell_j)K_{n_c} - K_{n_c}\ell_{n_c}]}{(\Sigma_j \ell_j)^2} & \dfrac{v_{n_c}}{(\Sigma v_j)^2}\cdots \\ \left[-H - (\Sigma_j \ell_j)\dfrac{\partial H^I}{\partial \ell_1}\right]\cdots & & \left[-H - (\Sigma_j \ell_j)\dfrac{\partial H^I}{\partial \ell_{n_c}}\right] & \left[-h - (\Sigma_j v_j)\dfrac{\partial h^I}{\partial v_1}\right]\cdots \end{bmatrix}$$

$$\begin{matrix} 0 & 0 & 0 \\ -1 & 0 & 0 \\ \ddots & & \vdots \\ & -1 & 0 \\ \dfrac{v_1}{(\Sigma_j v_j)^2}\cdots & \dfrac{v_1}{(\Sigma_j v_j)^2} & \dfrac{\ell_1}{(\Sigma_j \ell_j)} K_1 \left(\dfrac{\partial \ln f_1^0}{\partial T}\right) \\ \ddots & \vdots & \vdots \\ & \dfrac{[-\Sigma_j v_j + v_{n_c}]}{(\Sigma_j v_j)^2} & \dfrac{\ell_{n_c}}{(\Sigma_j \ell l_j)} K_{n_c} \left(\dfrac{\partial \ln f_{n_c}^0}{\partial T}\right) \\ & \left[-h - (\Sigma_j v_j)\dfrac{\partial h^I}{\partial v_{n_c}}\right] & -\Delta \end{matrix} \qquad (5)$$

where $\Delta = -(\Sigma_j \ell_j)\partial H^I/\partial T - (\Sigma_j v_j)\partial h^I/\partial T$

and

$$A(x) = \begin{bmatrix} 0 & \cdots & & 0 \\ 0 & \cdots & & 0 \\ \dfrac{\ell_1 K_1}{(\Sigma_j \ell_j)}\left(\dfrac{\partial \ln \gamma_1}{\partial \ell_1}\right)\cdots & \dfrac{\ell_1 K_1}{(\Sigma_j \ell_j)}\left(\dfrac{\partial \ln \gamma_1}{\partial \ell_{n_c}}\right) & 0 \ \ldots \ 0 & \Omega_1 \\ \vdots & \vdots & \vdots \quad \vdots & \vdots \\ \dfrac{\ell_{n_c} K_{n_c}}{(\Sigma_j \ell_j)}\left(\dfrac{\partial \ln \gamma_{n_c}}{\partial \ell_1}\right)\cdots & \dfrac{\ell_{n_c} K_{n_c}}{(\Sigma_j \ell_j)}\left(\dfrac{\partial \ln \gamma_{n_c}}{\partial \ell_{n_c}}\right) & 0 \ \ldots \ 0 & \Omega_{n_c} \\ (\Sigma_j \ell_j)\dfrac{\partial H^E}{\partial \ell_1}\cdots & (\Sigma_j \ell_j)\dfrac{\partial H^E}{\partial \ell_{n_c}} & 0 \ \ldots \ 0 & \psi \end{bmatrix} \qquad (6)$$

where

$$\Omega_i = \frac{\ell_i}{\left(\sum_j \ell_j\right)} K_i \left[\frac{\partial \ln\gamma_i}{\partial T} - \frac{\partial \ln\phi_i}{\partial T}\right]$$

and

$$\psi = -\left(\sum_i \ell_j\right)\frac{\partial H^E}{\partial T} - \left(\sum_j v_j\right)\frac{\partial h^E}{\partial T}.$$

Also, f_i^0 is the pure component fugacity of component i, and H^I and h^I are the ideal enthalpies for the liquid and vapor phases respectively. Moreover, γ_i and ϕ_i denote the ith component activity and fugacity coefficients, and H^E and h^E are the excess enthalpies for the liquid and vapor phases.

Within the general framework of a computed and approximated part we can define various Newton-based fixed-point methods. However, the two algorithms which are germane to the arguments that follow are Newton's method and the hybrid method. Briefly, they are defined as follows. If $A(x)$ is computed by finite differences, then we have a finite-difference implementation of Newton's method. If, on the other hand, $A(x)$ is computed by the rule

$$A_{k+1} = A_k + \sum_{i=1}^{n} (s_i^T s_i)^+ e_i^T [y - C_{k+1}s - A_k s] e_i s_i^T, \quad (7)$$

which is simply a modified form of the Schubert update, then we have the hybrid method. Here A_k and A_{k+1} are successive approximations to $A(x)$; $s = x_{k+1} - x_k$; $y = f(x_{k+1}) - f(x_k)$; and $C_{k+1} = C(x_{k+1})$. Moreover, s_i is the vector formed from s such that it has zeros everywhere the ith row of $A(x)$ does; e_i is the ith unit vector; and the subscripts T and $+$ denote matrix transposition and the generalized inverse, respectively. Finally, k is an iteration counter, and n is the total number of model equations.

It is well-known from thermodynamics that the functions $\ln\gamma_i$ and H^E are homogeneous functions of degree zero in mole numbers. That is,

$$\sum_{j=1}^{n_c} \left(\frac{\partial \ln\gamma_i}{\partial \ell_j}\right) \ell_j = 0, \quad i = 1,2,\ldots,n_c \quad (8)$$

and

$$\sum_{j=1}^{n_c} \left(\frac{\partial H^E}{\partial \ell_j}\right) \ell_j = 0. \quad (9)$$

Furthermore, because the lower $(n_c + 1) \times n_c$ partition of $A(x)$ defined by Eq. 6 contains only scalar multiples of the quantities $(\partial \ln\gamma_i/\partial \ell_j)$ for $i = 1,2,\ldots,n_c$ and $(\partial H^E/\partial \ell_j)$, it follows that $A(x)$ carries the vector $z = (\ell_1,\ell_2,\ldots,\ell_{n_c},0,0,\ldots 0)^T$ into the zero vector or that $A(x)$ annihilates z. In other words, $A(x)$ has a null space (or kernel) defined by the liquid phase component molal flow rates. We remark here that the vector z is of length $2n_c + 1$.

As stated earlier, when $A(x)$ is calculated by finite differences it has this null space at each iteration of the calculations. This is simply due to the fact that finite differencing provides thermodynamically consistent approximations to these partial derivatives. However, when the modified form of the Schubert update is used to build approximations to $A(x)$, such approximations do not usually have the null space containing z and are therefore thermodynamically inconsistent. This is because there are no provisions in the derivation of the update defined by Eq. 7 that force it to have the correct null space.

In the next section, we present a new quasi-Newton formula to be used in the context of the hybrid method that is nonsymmetric, satisfies the appropriate secant condition, and also guarantees that the current representation of the approximated part of the Jacobian matrix has the correct null space. In other words, the new updating formula builds thermodynamically consistent approximations to the approximated part of the Jacobian. It also satisfies the desired sparsity conditions.

A NEW QUASI-NEWTON FORMULA WITH A PRESCRIBED NULL SPACE

The usual way to derive quasi-Newton updates is to solve an appropriately posed variational calculus problem (e.g., see Dennis and Moré, 1977). Accordingly, in the full case, we seek the matrix approximation $\bar{A} = A_{k+1}$ that is closest to the previous approximation $A = A_k$ in the Frobenius matrix norm and such that it satisfies the overall secant condition and the null space constraint. We have neglected the sparsity conditions for the moment; we extend the results to the sparse case shortly. The variational problem that we wish to solve is given by

$$\min \|\bar{A} - A\|_F \quad (10)$$

$$\text{subject to } \bar{A}s = y - \bar{C}s \quad (11)$$

$$\text{and} \quad \bar{A}z = 0, \quad (12)$$

where $\|\cdot\|_F$ denotes the Frobenius matrix norm (i.e., $\|M\|_F = (\Sigma_i \Sigma_j m_{ij}^2)^{1/2}$) and s and y are defined as before. Also, $\bar{C} = C(x_{k+1})$, and z denotes any nonzero vector in the null space of $\bar{A}$. Furthermore, we suppose that z can be written in the form $z = \Sigma z^m$, where the set of vectors $\{z^1,z^2,\ldots,z^{n_k}\}$ forms a natural basis for the null space of $\bar{A}$, which has a dimension of n_k, and that $\bar{A}z^m = 0$ for $m = 1,2,\ldots,n_k$. Finally, we must require that s not be contained in the span of the set of vectors $\{z^1,z^2,\ldots,z^{n_k}\}$; otherwise the variational problem is ill-posed.

The solution to the variational problem defined by Eqs. 10 through 12 is given by

$$\bar{A} = A\left(I - \frac{zz^T}{z^Tz}\right) + \frac{(y - \bar{C}s - As)}{w^Ts} w^T + \left[\frac{s^Tz}{(z^Tz)(w^Ts)}\right] Azw^T, \quad (13)$$

where $w = s - (s^Tz/z^Tz)z$. This thermodynamically consistent quasi-Newton formula is derived in the appendix, along with proof of the fact that it satisfies both the secant condition and null space constraint.

To extend Eq. 13 to the sparse case, we need only include any sparsity conditions as additional constraints in the variational problem. More specifically, we pose the variational problem

$$\min \|\bar{A} - A\|_F \quad (14)$$

$$\text{subject to } \bar{A}s = y - \bar{C}s \quad (15)$$

$$\bar{A}z = 0 \quad (16)$$

$$\text{and} \quad \bar{a}_{ij} = 0, \quad (i,j)\epsilon I, \quad (17)$$

where I is the set of index pairs (i,j) for which the corresponding elements of $A(x)$ are known to be zero. Everything else is the same as before. The solution to this variational problem is

$$\bar{A} = A - \sum_{i=1}^{n} (z_i^T z_i)^+ (e_i^T Az) e_i z_i^T + \sum_{i=1}^{n} (w_i^T s_i)^+ e_i^T [y - \bar{C}s - As] e_i w_i^T + \sum_{i=1}^{n} (s_i^T z_i)(z_i^T z_i)^+ (w_i^T s_i)^+ (e_i^T Az) e_i w_i^T, \quad (18)$$

where $w_i = s_i - (s_i^T z_i / z_i^T z_i) z_i$

and where s_i and z_i are the vectors formed from s and z, respectively, such that they have zeros in each position that the ith row of $A(x)$ does. A discussion of the conditions necessary to guarantee that the variational problem defined by Eqs. 14 through 17, and thus the solution defined by Eq. 18, is well-defined is given in the appendix. Also contained there is proof of the fact that $\bar{A}$ defined by Eq. 18 satisfies the secant and null space conditions simultaneously. This last fact implies that the update defined by Eq. 18 is thermodynamically consistent.

We end this section with an algorithm for implementing the new formula within the context of the hybrid method together with a brief description of its steps and some comments pertinent to the problems in which we are interested.

A New Algorithm for the Hybrid Method

1. Start with x_o, A_o and a convergence tolerance $\epsilon > 0$. Also, set the iteration number $k = 0$.
2. Calculate $f(x_k)$.
3. Calculate $C_k = C(x_k)$.
4. Check the convergence conditions $\|f(x_k)\|_2 \leq \epsilon$. If it is satisfied, stop. Otherwise, go to step 5.
5. Set $B_k = C_k + A_k$ and solve the linear system $B_k s_k = -f(x_k)$ for s_k.
6. Set $x_{k+1} = x_k + s_k$.
7. Compute $f(x_{k+1})$ and C_{k+1}.
8. Define z and determine whether the secant condition and null space constraint constitute a linearly independent set of equations. If so, continue to step 9. If not, remove the ambiguous or redundant equation.
9. Calculate $y = f(x_{k+1}) - f(x_k)$ and update A_k using Eq. 18.
10. Set $k = k + 1$ and go to step 4.

The first step of the algorithm initializes the unknown variables, the approximated part of the Jacobian matrix, and the iteration counter. It also sets the convergence tolerance. Steps 2 and 3, on the other hand, calculate the values of the model equations and the computed part of the Jacobian matrix at the starting point x_o. Convergence is measured by the 2-norm of the vector function f and is checked in step 4 of the algorithm. The change in the unknown variables is calculated in step 5, which solves the linear system using Gaussian elimination in the form of an LDU factorization. Step 6 computes the new estimate of the solution by direct prediction, however line searching or a trust region strategy could easily be used. Step 7 calculates the values of the model equations and the computed part of the Jacobian matrix at this new estimate of the unknown variables. The null space is defined in step 8. Note that it can vary from one iteration to the next, which is the case in our applications. For example, for the single stage flash problem detailed earlier, the null space z is defined by $z = (\ell_1, \ell_2, \ldots, \ell_{n_c}, 0, \ldots, 0)^T_{k+1}$, where the subscript $k+1$ is used to indicate that the new estimate of the liquid component molal flow rates is used in this definition. Obviously, since these quantities are some of the unknown variables for the problem, they and the null space will change from one iteration to the next. Step 8 also ensures that the secant condition and null space constraint are neither ambiguous nor redundant (see the discussion in the appendix). We have not observed ambiguous or redundant constraints in practice. However, we felt it was important to include this check for completeness. Step 9 calculates an update to A using the new update, while step 10 increments the iteration counter and continues the main iterative loop.

In the next section we present some numerical results for this new quasi-Newton formula. In particular, we show that this new update can lead to solutions to separation problems for which the modified Schubert update fails.

PRELIMINARY NUMERICAL RESULTS

Although the new updating formula is theoretically superior to the modified Schubert update with regard to our applications, and thus brings the theoretical properties of the new hybrid method closer to those of Newton's method, it is not at all clear if exploiting the zero-degree homogeneity of the excess properties has any numerical consequence. Therefore, in this section we present the results of some preliminary numerical experiments using the new updating formula. More specifically, we compare this new updating formula, used within the context of the hybrid method, to a finite-difference Newton method and the original hybrid method on some chemical process design problems.

However, before presenting the results of our numerical study, we wish to clarify a few points. First, all of the methods that were studied used the same analytical first partial derivative information; the only difference between them was in the way in which the approximated part of the Jacobian was calculated. For example, for the finite-difference Newton method, A was calculated by finite differences at each iteration of the calculations. The original hybrid method, on the other hand, used the modified Schubert update to build approximations to $A(x)$. For the new hybrid method, one we call hybrid with null space, we used the new updating formula to build successive approximations to $A(x)$. Finally, all methods neglected the terms defined by

$$\Omega_i = \frac{\ell_i}{(\Sigma \ell_j)} K_i \left[\frac{\partial \ln \gamma_i}{\partial T} - \frac{\partial \ln \phi_i}{\partial T} \right].$$

The second point we wish to stress is that all of the methods were tested for robustness and computational efficiency using only the direct-prediction step. We did not use line searching or any trust region strategy. The reasons for this are as follows: When a direct-prediction Newton method is successful, which it is for many problems, line searching and trust region strategies usually only serve to increase the number of iterations and hence the computational work. At least that has been our experience on separation problems and we are unaware of any documented evidence to the contrary. Moreover, the success of a direct-prediction Newton method implies that the iterative approximations to the Jacobian matrix, which of course include the approximated parts, are good enough to give convergence. In fact, under these conditions the Jacobian matrix controls the performance of Newton's method completely. Therefore, since each method differs only in the way in which the approximated part of the Jacobian is calculated, it seemed reasonable to measure the relative goodness of these representations of the approximated parts in an environment in which they completely control numerical behavior (i.e., using direct prediction). Also, we did not scale any of the model equations, which were solved to an accuracy of 10^{-5}.

Finally, K-values and enthalpies were calculated using the UNIQUAC data base (Prausnitz et al., 1980) and all of the calculations were performed on an IBM 4341 computer in double-length arithmetic.

With these facts established, we present some numerical results for a single-stage, adiabatic flash problem. For this problem, the feed mixture consisted of 20 kgmol/s of ethanol and 40 kgmol/s of n-hexane. Furthermore, the feed pressure was varied from 3.039×10^5 to 20.260×10^5 Pa while the feed temperature was set at the corresponding bubble point temperature for the feed pressure under consideration. Finally, the pressure of the flash drum was fixed at 1.013×10^5 Pa. The numerical results are shown in Tables 1 and 2.

Before discussing the numerical results, we remark that the unknown variables for this problem were initialized as follows: We set $\ell_i = v_i = f_i/2$ for $i = 1,2, \ldots, n_c$, and used the feed temperature as the initial approximation to the equilibrium temperature of the flash drum. Note that the feed is bubble-point liquid. While this is a perfectly natural way to estimate the solution, it does not represent a particularly good starting point; in fact, it is a reasonably poor one. Moreover, for each of the hybrid methods we calculated the initial approximated part of the Jacobian matrix by finite differences. Starting with $A_o = 0$ gave very poor results for both hybrid methods. Finally, in tallying the rigorous thermodynamics calculations we counted each computation of a vector of K-values as one rigorous thermodynamic calculation and the determination of a liquid phase and vapor phase enthalpy each once. For this problem we assumed that the vapor phase fugacity coefficients and

TABLE 1. RESULTS FOR SINGLE STAGE FLASH CALCULATIONS

Feed Pressure p_f (10^5 Pa)	Number of Iterations: Finite-Difference Newton	Original Hybrid	Hybrid with Null Space
3.039	6	8	10
4.052	8	10	9
5.065	8	F	9
10.130	8	F	10
15.195	9	18	11
20.260	9	13	14

F = failure.

TABLE 2. RESULTS FOR SINGLE STAGE FLASH CALCULATIONS

Feed Pressure p_f (10^5 Pa)	Number of Rigorous Thermodynamics Calculations: Finite-Difference Newton	Original Hybrid	Hybrid with Null Space
3.039	48	29	35
4.052	64	35	32
5.065	64	NA	32
10.130	64	NA	35
15.195	72	59	38
20.260	72	44	47

NA = not applicable.

the vapor enthalpy of mixing were a function of temperature only.

As shown in Table 1, both the finite-difference Newton method and the new hybrid method (i.e., hybrid with null space) had no difficulty solving all of the problems within the set. The original hybrid method, on the other hand, failed on two problems within the set. Incidentally, the direct-prediction partial Newton method (i.e., $A_k = 0$ for each iteration) failed on all but one problem.

With regard to the failure of the original hybrid method we offer the following comments, in which draw upon our experience in solving many problems, not just those presented here. In some cases, these failures were caused by inordinately large temperature corrections at some juncture of the calculations, usually between two and five iterations. In other cases, extremely large changes in component molal flow rates were observed. Moreover, we made no effort to safeguard against unreasonable changes in the variables other than to prevent nonnegativity, and we have restricted our attention to the direct-prediction step only. However, the fact remains that the original hybrid method was unable to build representations of the approximated part of the Jacobian matrix that resulted in convergence, while the finite-difference Newton method and the hybrid method with null space were able to do so. Thus, we believe these latter methods build better approximations to $A(x)$.

Because the rigorous thermodynamics calculations can dominate the time required to solve a chemical process design problem with nonideal thermodynamics, it is usual to measure computational efficiency by counting the total number of rigorous physical properties calculations needed over the course of solution. When this was done for the flash problem under consideration, the hybrid method with the new updating formula was clearly superior, as shown in Table 2. It used between 27 and 47% fewer rigorous thermodynamics calculations than the finite-difference Newton method. Moreover, it generally was more efficient than the original hybrid method except for a few isolated cases.

In order to demonstrate that the modified Schubert update does not build approximations to $A(x)$ that satisfy the null space constraint, and also to show that the new updating formula can yield better representations to the approximated part of the Jacobian matrix than the modified Schubert update, we present some additional numerical evidence. More specifically, we show the respective approximations to $A(x)$ for the modified Schubert update, the finite-difference Newton method, and the new updating formula on the first, third, and ninth iterations for problem 5 in Table 1 (i.e., $p_f = 15.195 \times 10^5$ Pa). The nonzero entries of these matrices along with the corresponding values of z, where $z = (\ell_1, \ell_2, 0., 0., 0.)^T_{k+1}$, are shown in Table 3 to five significant digits.

First, observe that the approximated part of the Jacobian matrix generated by the modified Schubert update does not satisfy the null space constraint on any of the iterations displayed in Table 3, or for that matter any iteration of the calculations except the first. In contrast, the approximated parts generated by finite differencing and the new updating formula possess the correct kernel.

Second, notice that the new updating formula approximates $A(x)$ extremely well toward the end of the calculations. Clearly, the approximations to $A(x)$ generated by the new updating formula are much better than those generated by the modified Schubert update. This, in our opinion, is why the hybrid method with the null space restriction outperforms the original hybrid method on this problem, as well as some others that we have studied.

There is an interesting and simple modification of our new thermodynamically consistent updating formula (Eq. 18), which is based on the concept of iterated projections (see Dennis and Schnabel, 1979). More specifically, we can build a sparse and thermodynamically consistent approximation to $A(x)$ by simply iterating between the set of sparse, secant matrices and that are also annihilators of z, in that order. This idea results in the update defined by the tandem equations

$$\hat{A} = A + \sum_{i=1}^{n} (s_i^T s_i)^+ e_i^T [y - \bar{C}s - As] e_i s_i^T \tag{19}$$

and

$$\bar{A} = \hat{A} + \sum_{i=1}^{n} (z_i^T z_i)^+ e_i^T \hat{A} z e_i z_i^T, \tag{20}$$

which the experienced reader should recognize as just successive applications of Schubert's formula. The important point to note here is that the matrix $\bar{A}$, although thermodynamically consistent at each iteration, will only usually satisfy the secant condition in the limit. However, we do not view this as a difficulty since that is, in fact, precisely what Newton's method with finite differences does. We are currently testing this thermodynamically consistent update that comes from the idea of using iterated projections along with that defined by Eq. 18.

TABLE 3. APPROXIMATED PART OF JACOBIAN MATRIX FOR VARIOUS UPDATING STRATEGIES

Iteration No.	Modified Schubert Update	Finite-Difference Newton	New Formula
1	$\begin{bmatrix} -0.3908 & 0.1954 & 0 \\ 0.1526 & -0.0763 & 0 \\ 778.58 & 389.29 & -192.92 \end{bmatrix}$ (10, 20, 0, 0, 0)	$\begin{bmatrix} -0.3908 & 0.1954 & 0 \\ 0.1526 & -0.0763 & 0 \\ 778.58 & -389.29 & -192.92 \end{bmatrix}$ (10, 20, 0, 0, 0)	$\begin{bmatrix} -0.3908 & 0.1954 & 0 \\ 0.1526 & -0.0763 & 0 \\ 778.58 & -389.29 & -192.92 \end{bmatrix}$ (10, 20, 0, 0, 0)
3	$\begin{bmatrix} -0.3692 & 0.1335 & 0 \\ 0.5726 & -0.0912 & 0 \\ 12{,}762. & -2{,}044.7 & 26{,}680. \end{bmatrix}$ (13.075, 0, 0, 0, 0)	$\begin{bmatrix} -0.0192 & 0.0232 & 0 \\ 0.0353 & -0.0426 & 0 \\ 422.73 & -510.59 & -215.36 \end{bmatrix}$ (14.590, 12.080, 0, 0, 0)	$\begin{bmatrix} -0.0109 & 0.0660 & 0 \\ 0.0493 & -0.2985 & 0 \\ 145.46 & -881.65 & -84.584 \end{bmatrix}$ (29.753, 4.9090, 0, 0, 0)
9	$\begin{bmatrix} 0.0407 & 0.0716 & 0 \\ 0.0252 & -0.0425 & 0 \\ -3{,}074.8 & 3{,}805.4 & 7{,}179.7 \end{bmatrix}$ (14.261, 10.353, 0, 0, 0)	$\begin{bmatrix} -0.0240 & 0.0121 & 0 \\ 0.0244 & -0.0123 & 0 \\ 771.72 & -388.95 & -272.49 \end{bmatrix}$ (8.3303, 16.528, 0, 0, 0)	$\begin{bmatrix} -0.0247 & 0.0124 & 0 \\ 0.0259 & -0.0130 & 0 \\ 764.77 & -385.44 & -301.64 \end{bmatrix}$ (8.3303, 16.528, 0, 0, 0)

With the exception that the null rows and columns have been removed, these matrices correspond to the one defined by Eq. 6.
The last row of each matrix has been multiplied by 10^{-3} for convenience.

SUMMARY

We have introduced a new quasi-Newton updating formula for use in the context of the hybrid method of chemical process design. This new update exploits the zero-degree homogeneity of the nonideal thermodynamic functions (i.e., H^E and $\ln\gamma$) that are usually involved in multicomponent separation processes involving nonideal phase equilibria. We showed that this zero-degree homogeneity gives rise to a natural null space (or kernel) for the approximated part of the Jacobian matrix which is defined by the component molal flow rates. Using this fact, we derived a new quasi-Newton updating formula that gives this correct null space to the sequence of approximated parts, in addition to satisfying the overall secant condition and sparsity constraints. Finally, we demonstrated that this new updating formula can result in better numerical performance than the modified Schubert update. In some cases it can result in the solution to a problem for which the modified Schubert update causes failure. However, we must temper this statement by noting that we do not as yet have sufficient experience with either the original hybrid method or the new updating formula presented here to make any definitive statement concerning the superiority of one of these updates in comparison to the other. We may never be able to do this, but it is not altogether clear that it matters.

APPENDIX: DERIVATION OF A THERMODYNAMICALLY CONSISTENT QUASI-NEWTON FORMULA

In this appendix we derive a new thermodynamically consistent quasi-Newton formula by variational calculus. We also discuss the conditions under which both the variational problem and its solution are well-defined. Finally, we extend this result and the related discussions to the sparse case.

In the full case, we wish to solve the variational problem given by

$$\min\|\bar{A} - A\|_F \tag{A1}$$

subject to $\bar{A}s = y - \bar{C}s$ (A2)

and

$$\bar{A}z = 0, \tag{A3}$$

where $\|\cdot\|_F$ denotes the Frobenius matrix norm (i.e., $\|M\|_F = (\Sigma_i \Sigma_j m_{ij}^2)^{1/2}$, and $s = x_{k+1} - x_k$, and $y = f(x_{k+1}) - f(x_k)$. Also, $\bar{C} = C(x_{k+1})$, and z denotes any nonzero vector in the null space of $\bar{A}$. We note that Eq. A2 is called the secant equation and that Eq. A3 is a composite thermodynamic or zero-degree homogeneity constraint. Furthermore, we suppose that z can be written in the $z = \Sigma_{m=1}^{n_k} z^m$, where the set of vectors $\{z^1, z^2, \ldots, z^{n_k}\}$ forms a natural and mutually orthogonal basis for the null space of $\bar{A}$, and where n_k is the dimension of that kernel. We also assume that $\bar{A}z^m = 0$ for $m = 1,2,\ldots,n_k$. Finally, we require that s lie outside the subspace spanned by the set $\{z^1, z^2, \ldots, z^{n_k}\}$, written $s \notin [z^1, z^2, \ldots, z^{n_k}]$; otherwise the variational problem is ill-posed. These hypotheses are usually easy to satisfy for the problems in which we are interested.

It changes nothing and is primarily a convenience to write the variational problem defined by Eqs. A1 through A3 as

$$\min \frac{1}{2}\|\bar{A} - A\|_F^2 \tag{A4}$$

subject to $\bar{A}s = y - \bar{C}s$ (A5)

$$\bar{A}z = 0. \tag{A6}$$

To solve this problem, we first form the Lagrangian function given by

$$L = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}(\bar{a}_{ij} - a_{ij})^2 - \sum_{i=1}^{n}\lambda_i\left[\sum_{j=1}^{n}\bar{a}_{ij}s_j - e_i^T(y - \bar{C}s)\right] - \sum_{i=1}^{n}\hat{\lambda}_i\left[\sum_{j=1}^{n}\bar{a}_{ij}z_j\right].$$

The solution lies at the stationary point of L which is defined by

$$\frac{\partial L}{\partial \bar{a}_{ij}} = \bar{a}_{ij} - a_{ij} - \lambda_i s_j - \hat{\lambda}_i z_j = 0, \quad i,j = 1,2,\ldots,n$$

$$\frac{\partial L}{\partial \lambda_i} = \sum_{j=1}^{n}\bar{a}_{ij}s_j - e_i^T(y - \bar{C}s) = 0, \quad i = 1,2,\ldots,n$$

and

$$\frac{\partial L}{\partial \hat{\lambda}_i} = \sum_{j=1}^{n}\bar{a}_{ij}z_j = 0, \quad i = 1,2,\ldots,n.$$

In matrix notation, this gives

$$\bar{A} - A - \lambda s^T - \hat{\lambda}z^T = 0 \tag{A7}$$

$$\bar{A}s - (y - \bar{C}s) = 0 \tag{A8}$$

$$\bar{A}z = 0. \tag{A9}$$

Multiplying Eq. A7 by z and making use of Eq. A9 allows us to establish a relationship between $\hat{\lambda}$ and λ. That is, $0 = \bar{A}z - Az - \lambda s^T z - \hat{\lambda}z^T z = -Az - \lambda s^T z - \hat{\lambda}z^T z$, which implies that

$$\hat{\lambda} = -\frac{s^T z}{z^T z}\lambda - \frac{Az}{z^T z}. \tag{A10}$$

Using Eq. A10 in Eq. A7 gives $\bar{A} - A - \lambda s^T - (-s^T z/z^T z\lambda - Az/z^T z)z^T = 0$, which, after some algebra, is

$$\bar{A} - A\left(I - \frac{zz^T}{z^T z}\right) - \lambda w^T = 0, \tag{A11}$$

where $w = s - (s^T z/z^T z)z$.

Equations A11 and A8 allow us to find an expression for λ. Multiplying Eq. A11 by s and using Eq. A8 gives $0 = \bar{A}s - A(I - zz^T/z^T z)s - \lambda w^T s = y - \bar{C}s - As + s^T z/z^T z Az - \lambda w^T s$, which implies that

$$\lambda = \frac{(y - \bar{C}s - As)}{w^T s} + \frac{s^T z}{(z^T z)(w^T s)}Az. \tag{A12}$$

Finally, using Eq. A12 in Eq. A11 gives

$$\bar{A} = A\left(I - \frac{zz^T}{z^T z}\right) + \frac{(y - \bar{C}s - As)}{w^T s}w^T + \left[\frac{s^T z}{(z^T z)(w^T s)}\right]Azw^T, \tag{A13}$$

where as before, $w = s - (s^T z/z^T z)z$.

Note that since $w^T z = s^T z - (s^T z/z^T z)z^T z = 0$ and $(I - zz^T/z^T z)z = 0$, because $(I - zz^T/z^T z)$ projects orthogonally to z, it follows that Eq. A13 satisfies the null space constraint. Moreover,

$$\begin{aligned}\bar{A}s &= A\left(I - \frac{zz^T}{z^T z}\right)s + \frac{(y - \bar{C}s - As)}{w^T s}w^T s + \left[\frac{s^T z}{(z^T z)(w^T s)}\right]Azw^T s \\ &= As - \left(\frac{s^T z}{z^T z}\right)Az + y - \bar{C}s - As + \left(\frac{s^T z}{z^T z}\right)Az \\ &= y - \bar{C}s\end{aligned}$$

and thus Eq. A13 also satisfies the secant condition. Hence, $\bar{A}$ is, in fact, the closest matrix to A in the Frobenius norm that satisfies the overall secant condition and the null space constraint.

The reason we must require that s lie outside the span of the set of vectors $\{z^1, z^2, \ldots, z^{n_k}\}$ is to avoid either redundant or ambiguous constraints in the variational problem. To see this, suppose $s \in [z^1, z^2, \ldots, z^{n_k}]$ with $s \neq 0$ and $z^m \neq 0$ for $m = 1, 2, \ldots, n_k$. This means that $s = \Sigma_{m=1}^{n_k}\alpha^m z^m$ for some set of scalars $\{\alpha^1, \alpha^2, \ldots, \alpha^{n_k}\}$ such that at least one α^m is nonzero.

Observe also that the null space constraint can be written as

$$\bar{A}z^m = 0, \qquad m = 1,2,\ldots,n_k \tag{A14}$$

since $z = \Sigma_m z^m$ and $\{z^1, z^2, \ldots, z^{n_k}\}$ form a basis for the null space of $\bar{A}$. Furthermore, because $s \in [z^1, z^2, \ldots, z^{n_k}]$ and because the set of vectors $\{z^1, z^2, \ldots, z^{n_k}\}$ is mutually orthogonal, it follows that the secant condition can be written as

$$\alpha^m \bar{A} z^m = r^m, \qquad m = 1,2,\ldots,n_k \tag{A15}$$

where $\Sigma_m r^m = y - \bar{C}s$ and where the actual form of the individual vectors r^m for $m = 1,2,\ldots,n_k$ is, as we show, unimportant.

If $r^m = 0$, which is not usually the case, then Eqs. A14 and A15 imply that the secant equation and null space constraint are redundant. If, on the other hand, $r^m \neq 0$, then the secant condition and null space equation constitute an ambiguous set of constraints for the variational problem.

Finally, because these conditions of constraint redundancy and ambiguity arise from supposing that $s \epsilon [z^1, z^2, \ldots, z^{n_k}]$, it is clear that we must require that s lie outside the span of $\{z^1, z^2, \ldots, z^{n_k}\}$.

In the sparse case, we wish to solve the variational problem given by

$$\min \frac{1}{2} \|\bar{A} - A\|_F^2 \tag{A16}$$

$$\text{subject to } \bar{A}s = y - \bar{C}s \tag{A17}$$

$$\bar{A}z = 0 \tag{A18}$$

$$\text{and} \qquad \bar{a}_{ij} = 0, \ (i,j) \epsilon I, \tag{A19}$$

where I is the set of index pairs (i,j) for which the corresponding elements of $A(x)$ are known to be zero. Everything else is the same as before.

Because $A(x)$ is nonsymmetric, it is convenient to consider each row of the update separately. Thus we need only concern ourselves with, say, the ith row of A. Now the usual way to account for sparsity is to form the appropriate projections of s and z, call them s_i and z_i. In particular, we define s_i and z_i to be the vectors formed from s and z, respectively, such that they have zeros in each location that the ith row of $A(x)$ does. However, here we must be a little bit more careful than in the case of the Schubert update. In order to insure that the variational calculus problem defined by Eqs. A16 through A19 is well-posed, we must require that $s_i \notin [z_i^m : z_i^m \neq 0$ and linearly independent, $1 \leq m \leq n_k]$. This precaution avoids both ambiguous and redundant constraints. For example, suppose $s_i \epsilon [z_i^m : z_i^m \neq 0$ and linearly independent, $1 \leq m \leq n_k]$. This implies that $s_i = \Sigma_m \alpha^m z_i^m$ for some set of scalars. Moreover, suppose $e_i^T[(y - \bar{C}s)] = 0$. Then in this case for row i the secant condition and the null space constraint are redundant. If, on the other hand, $s_i \epsilon [z_i^m : z_i^m \neq 0$ and linearly independent, $1 \leq m \leq n_k]$ and $e_i^T[(y - \bar{C}s)] \neq 0$, then the secant condition and the null space constraint are ambiguous.

The other point we wish to make, assuming that $s_i \notin [z_i^m : z_i^m \neq 0$ and linearly independent, $1 \leq m \leq n_k]$ is that the conditions s_i, z_i^m and $e_i^T(y - \bar{C}s) \neq 0$, which are usual, together with the overall secant condition and null space constraint impose a slight restriction on the set of admissible sparsity patterns for the ith row of $\bar{A}$. In particular, under these conditions $\bar{A}$ must have at least $M + 1$ possible nonzero entries in the ith row, where M denotes the number of projections z_i^m that are nonzero, in order to simultaneously satisfy both the secant and null space constraints. However, this restriction does not present any difficulties for the problems in which we are interested. Even for a binary mixture with nonideal liquid phase behavior there are at least $2M$ nonzero entries for each of the rows corresponding to the equilibrium and energy balance equations.

With these facts established, and under the assumption that they hold true, the solution to the variational problem defined by Eqs. A16 through A19 proceeds, for the most part, as before. The only real difference is the bookkeeping that is necessary to fix the desired sparsity pattern. Accordingly, the solution is given by the rule

$$\begin{aligned}\bar{A} = A &- \sum_{i=1}^{n} (z_i^T z_i)^+ (e_i^T A z) e_i z_i^T \\ &+ \sum_{i=1}^{n} (w_i^T s_i)^+ e_i^T [y - \bar{C}s - As] e_i w_i^T \\ &+ \sum_{i=1}^{n} (s_i^T z_i)(z_i^T z_i)^+ (w_i^T s_i)^+ (e_i^T A z) e_i w_i^T, \end{aligned} \tag{A20}$$

where $w_i = s_i - (s_i^T z_i / z_i^T z_i) z_i$. Moreover, it is easy to show that the sparse update defined by Eq. A20 satisfies the overall secant condition and the null space constraint by simply checking these conditions for the ith row. That is, since $w_i^T z_i = s_i^T z_i - (s_i^T z_i / z_i^T z_i) z_i^T z_i = 0$, $z_i^T z = z_i^T z_i$ and $e_i^T A z = e_i^T A z_i$, it follows that

$$\begin{aligned} e_i^T \bar{A} z &= e_i^T A z - (z_i^T z_i)^+ (e_i^T A z)(z_i^T z) \\ &\quad + (w_i^T s_i)^+ e_i^T [y - \bar{C}s - As](w_i^T z) \\ &\quad + (s_i^T z_i)(z_i^T z_i)^+ (w_i^T s_i)^+ (e_i^T A z)(w_i^T z) \\ &= e_i^T A z - (z_i^T z_i)^+ (e_i^T A z)(z_i^T z_i) = 0. \end{aligned}$$

Hence, the null space constraint is satisfied for row i, and since i was arbitrary it follows that $\bar{A}$ defined by Eq. A20 annihilates z. Furthermore, we have that

$$\begin{aligned} e_i^T \bar{A} s &= e_i^T A s - (z_i^T z_i)^+ (e_i^T A z)(z_i^T s) \\ &\quad + (w_i^T s_i)^+ e_i^T [y - \bar{C}s - As](w_i^T s) \\ &\quad + (s_i^T z_i)(z_i^T z_i)^+ (w_i^T s_i)^+ (e_i^T A z)(w_i^T s) \\ &= e_i^T A s - (z_i^T z_i)^+ (e_i^T A z)(z_i^T s_i) \\ &\quad + e_i^T [y - \bar{C}s - As] + (s_i^T z_i)(z_i^T z_i)^+ (e_i^T A z) \\ &= e_i^T A s + e_i^T [y - \bar{C}s] - e_i^T A s \\ &= e_i^T [y - \bar{C}s], \end{aligned}$$

which shows that row i of $\bar{A}$ satisfies the overall secant condition. Moreover, since row i was arbitrary, it follows that $\bar{A}$ defined by Eq. A20 satisfies $\bar{A}s = y - \bar{C}s$.

NOTATION

A_k	= approximated part of Jacobian matrix at kth iteration
B_k	= Jacobian approximation at kth iteration
C_k	= computed part of Jacobian matrix at kth iteration
e_i	= ith unit vector
f, f_i, f_i^o	= vector function of model equations, molal flow rate for ith component of feed, standard state fugacity of pure component i
h, h^I, h^E	= vapor phase enthalpy, ideal enthalpy, enthalpy of mixing
H, H_f, H^I, H^E	= liquid phase enthalpy, enthalpy of feed, ideal enthalpy, excess enthalpy
J	= Jacobian matrix of f
K_i	= equilibrium ratio for the ith component
p_f	= feed pressure
Q	= heat duty
s, s_k	= change in the independent variables, at kth iteration
T, T_f	= temperature, feed temperature
v_i	= ith component vapor molal flow rate
w	= projection of s orthogonal to null space
x, x_k	= vector of unknown variables, at kth iteration
y	= change in vector function f from one iteration to the next
z	= vector contained in the iterative null space for approximated part of the Jacobian matrix

Script

ℓ_i	= liquid phase molal flow rate for the ith component

Greek Letters

γ_i	= ith component liquid phase activity coefficient
ϵ	= convergence tolerance
$\lambda\hat{\lambda}$	= vector of Lagrange multipliers for overall secant condition, for null space constraint
ϕ_i	= vapor phase fugacity coefficient for ith component

Subscripts

i,j	= component number
k	= iteration counter

Superscripts

o	= standard state
T	= transpose
$+$	= pseudoinverse

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Manuscript received Oct. 14, 1983; revision received Mar. 1, 1984, and accepted Mar. 4.